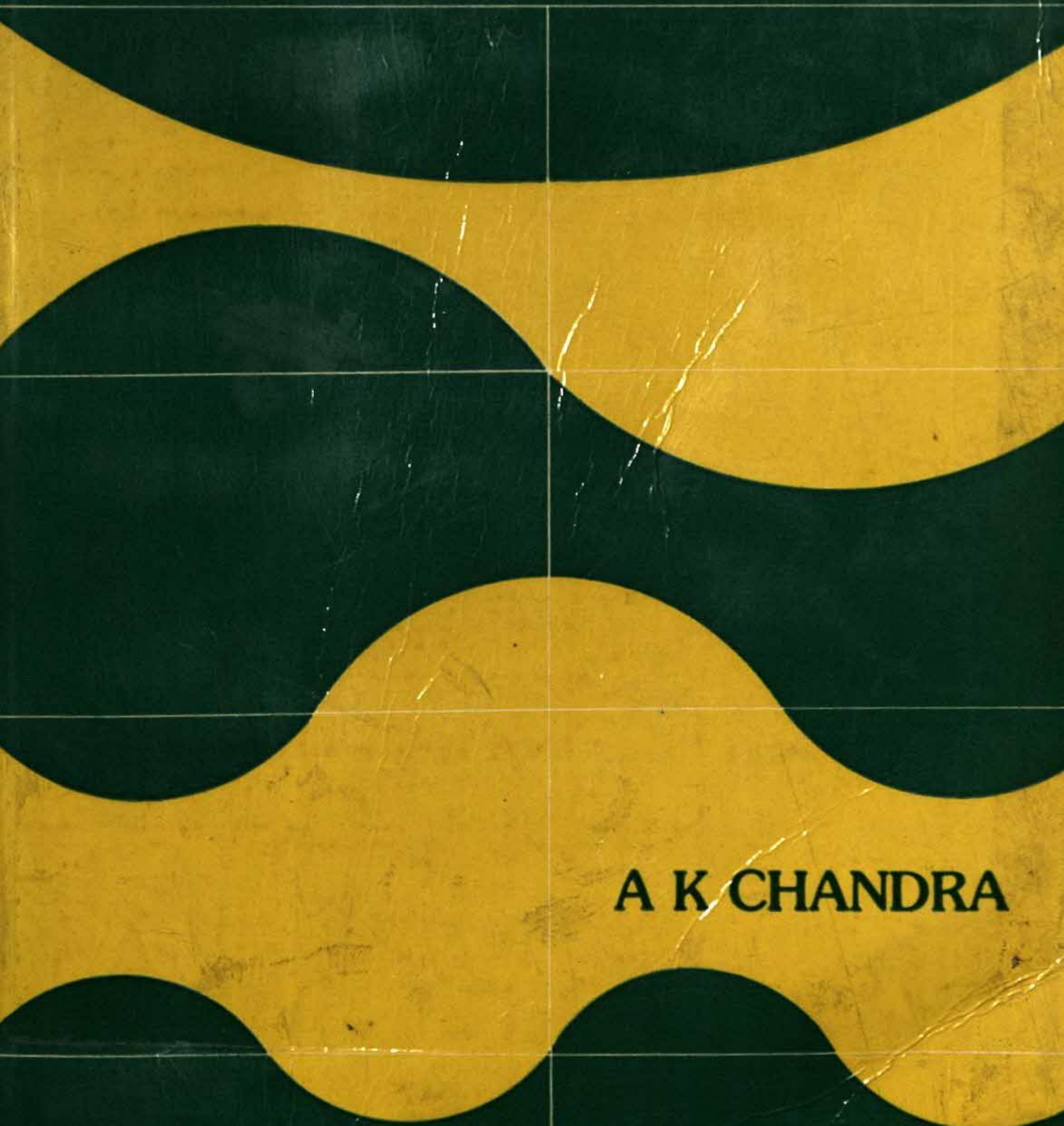
INTRODUCTORY QUANTUM CHEMISTRY

THIRD EDITION



A K CHANDRA

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INTRODUCTORY QUANTUM CHEMISTRY

Third Edition

Introductory Quantum Chemistry

Third Edition

A K Chandra
Indian Institute of Science
Bangalore

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Preface to the Third Edition

Whenever a teacher teaches a course every year for many years an evolutionary change in the course takes place. If he follows a particular book for his course, his course will no longer be as closely related to that book as it was before. This is one of the reasons for revising the book. Besides, new material is added at appropriate places in relevant chapters in order to keep up with the revised curricula. These extensions in coverage are also treated at an introductory level so that the title of the book remains the same. This book is primarily meant for studies at the postgraduate level in the Indian universities. It can also be used by the senior undergraduate students in USA, Europe and Japan.

Among the extensions in coverage the concept of tensor, for example, is introduced at an introductory level in Chapter 3 (Appendix 3B) as the students deal with properties such as moment of inertia, quadrupole moment, etc. This book, therefore, differs from earlier books (for example, *Quantum Chemistry* by Eyring, Walter and Kimball, Wiley, 1944) where vectors and determinants were introduced at the elementary level. I feel now that these are too well known to be given in a book primarily meant for the postgraduate students.

Several chapters have been thoroughly revised. For example, Chapter 7 is completely rewritten. Chapter 10 on Semiempirical and Ab initio Theories is a new chapter and gives the detailed technology of the molecular orbital calculations. Chapter 11 (Chapter 10 in the previous edition) is rewritten with the latest advances in the applications of the Hellmann-Feynman theorem in chemistry. Treatment of chemical bonding cannot be complete without a discussion of the force concept in chemistry. Most books on quantum chemistry, however, avoid the detailed applications of the Hellmann-Feynman theorem to chemical bonding and molecular structure. Teachers also avoid dealing with the force concept. I have now tried to equip this new edition with the pedagogic paraphernalia.

I would like to thank my students and colleagues at the Department of Inorganic and Physical Chemistry. My special thanks go to Dr Saraswati Vishveshwara of the Molecular Biophysics Unit for going through Chapter 10. My sincere thanks are due to Prof. M S Gopinathan, Indian Institute of Technology, Madras, who read several chapters, especially those which underwent thorough revision. Thanks are also due to Prof. N F Stepanov, Moscow State University, Moscow for his critical reading of Chapters 10 and 11, when he was here as a Visiting Scientist.

Finally, I would like to record my appreciation for the assistance of Mr S Srirama who typed the manuscript and Mr Venugopal for preparing the diagrams.

A K CHANDRA

Preface to the Second Edition

It is gratifying to note that most chapters in this book have received endorsement by a considerable number of students and teachers of various universities in India. I am grateful to all who have written to me, some drawing attention to minor errors and other suggesting addition of a few more chapters on certain special topics. Most of them strongly recommended including a chapter on "Symmetry". This new edition has, therefore, a chapter on the principles of symmetry and their applications in chemistry. Besides, a few additions, such as the simple Hückel treatment of the cyclic conjugated systems and aromaticity have been incorporated in Chapter 8. For the new chapter a set of problems are given and worked out in detail in the "Answers to the Problems" section. These problems are so chosen as to supplement the knowledge already acquired by the reader from the text.

I would like to thank my colleagues Dr D N Sathyanarayana and Prof. K. Venkatesan for their careful reading of the new chapter (Chapter 9) and making several critical suggestions. Finally, I would like to record my appreciation of the assistance of Mr S Srirama who typed the manuscript and Mr Venugopal for preparing the diagrams.

A K CHANDRA

Preface to the First Edition

When I started writing this manuscript, I did not have the honest intention of ever completing this for a university level textbook on quantum chemistry. Thanks are due to the University Grants Commission (Government of India) not only for providing me with enough funds for the preparation of the manuscript but also for their asking me to submit progress reports every six months. I found a great difficulty in writing a progress report for them without making any real progress in this work.

The basic material of this book is based on my lectures to the postgraduate students in the Department of Pure Chemistry, Calcutta University, for several years, in the Department of Chemistry, Indian Institute of Technology, Bombay, for a year or so, and at present in the Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore. This book is therefore primarily intended for students of chemistry at the M.Sc. level in India, and possibly at the senior undergraduate levels in the British and American universities. Teachers and research workers who are not actively engaged in this particular field of chemistry but wish to keep up with the recent trends in chemical education will find this book very useful. This book contains chapters that are basic to an understanding of the important concepts that quantum mechanics has introduced in chemistry. Since an adequate and critical comprehension can only be achieved if they are presented in mathematical language, considerable efforts have been made to make the mathematics simple and comprehensive. However, I have assumed that a typical reader has been exposed at some time to an introductory course in physics, calculus, vectors and determinant.

This book covers the most 'recent advances' in this field in various chapters, especially in the last two chapters which explain the Woodward-Hoffmann rule and describe the chemical applications of the Hellmann-Feynman theory. These are important and significant topics, and at the same time simple enough for a typical reader to follow.

Every chapter, except the last one, is followed by a set of problems most of which are worked out in detail in the 'Answers to the Problems' section. These problems are chosen so as to supplement the knowledge already acquired by the reader from the text.

My sincere thanks are due to Dr. N.G. Mukherjee, Calcutta University, and Dr. B.M. Deb, Indian Institute of Technology, Bombay. Dr. Mukherjee read the entire manuscript in depth, made many suggestions for improvement and suggested many problems for several chapters of this book, while Dr. Deb was the main author of the chapter on the Hellmann-Feynman theorem and some of its chemical applications. I would like to thank Dr. C.D. Flint, Birkbeck College, London University, for his careful reading of the chapters 5, 6 and 7 and making several critical suggestions when he was here as a visiting scientist. Thanks are due to Professor P.T. Narasimhan, Indian Institute of Technology, Kanpur, for his critical reading of the Chapters 3 and 4 and pointing out many obscurities in the previous version of these two chapters. Although various scholars, including my own students (Dr. D.C. Mukherjee of Calcutta University, and Mr. R. Sundar and Mr. B.S. Sudhindra, both of the Indian Institute of Science, Bangalore) have gone through some portions of this book, it is too much to hope that this book is free from any errors and obscurities. But the responsibility for these is entirely mine, and I shall be grateful to be told of the places where I could do better.

I could not end this Preface without an acknowledgement to the several lecture courses which I followed during my stay at Oxford, especially those of late Prof. C.A. Coulson, F.R.S., whose ideas and derivations may be found in several pages of this book. However, I feel, my greatest debt goes to my teacher, Prof. Sadhan Basu, Palit Professor of Chemistry, Calcutta University, whose lectures on various topics of quantum chemistry on various occasions at the University College of Science, Calcutta, when I was one of his pupils, created in me an immense interest in this field. Prof. A.B. Biswas, Indian Institute of Technology, Bombay, had the great kindness to advise me with many helpful suggestions concerning the plan and emphasis of this book. I would also like to thank Prof. Satish Dhawan, Director, and Prof. A.R. Vasudeva Murthy, Chairman of the Division of Chemical and Biological Sciences, Indian Institute of Science, for their positive encouragement and general help in this endeavour.

Finally, I would like to record my appreciation of the assistance of Mr. C.R. Sreenivasa Murthy who carefully typed and retyped the entire manuscript, and of my wife, Bani, for reading the proofs.

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1

Introduction: Waves and Quanta

1.1 Wave and Particle Nature of Radiation

Radiation is known to be composed of electromagnetic waves with electric and magnetic fields perpendicular to each other and perpendicular to the direction of propagation. By definition, wavelength λ is the distance between the successive crests and the phase velocity ω is the velocity at which a given crest moves (Fig. 1.1).

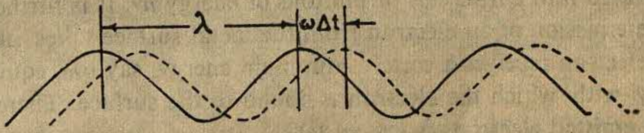

Fig. 1.1 *Electromagnetic wave at time t and t + Δt*

There are quite a number of optical phenomena, notably the diffraction and the interference of radiation, which provide the strong evidence in favour of the wave nature of radiations.

There are, however, two other phenomena which provide equally strong evidence in favour of the particle nature of radiation. They are the photoelectric effect and the Compton scattering. In the photoelectric effect electrons are emitted from a metal surface illuminated by the ultraviolet radiation. If the kinetic energy (KE) of the emitted electrons is plotted against the frequency $\nu(= c/\lambda$, where c is the velocity of light) of the incident radiation, a graph of the type shown in Fig. 1.2 is obtained. It has been observed that increasing the intensity of the incident radiation at constant frequency does not affect the KE of the emitted electrons but increases the number of electrons emitted in unit time. The equation of the straight line shown in Fig. 1.2 is

$$\text{KE} = h(\nu - v_0) \tag{1.1}$$

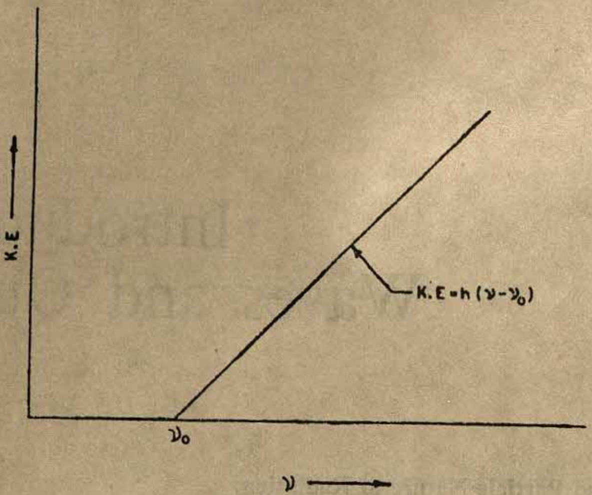

Fig. 1.2 *Kinetic energy of photoelectrons*

where ν_0 is the minimum frequency below which no electron is emitted and h is called the Planck constant. This photoelectric phenomenon was explained by Einstein using Planck's quantum hypothesis that the energy of radiation is not distributed through waves, as the classical concept leads to, but is concentrated into corpuscles or photons of energy $h\nu$. It is further assumed that the emission of an electron from the metal surface takes place only when the electron receives a certain minimum energy, say $h\nu_0$, equivalent to the energy with which the electron is bound to the surface. Therefore, the KE of the emitted electrons is $h(\nu - \nu_0)$.

Since the energy E of a photon, according to Planck, is given by

$$E = h\nu \tag{1.2}$$

and the mass, m of the photon can be calculated using Einstein's relativistic equation

$$E = mc^2 \tag{1.3}$$

where c is the velocity of light, the momentum p of a photon is given by

$$p = mc \tag{1.4}$$

This momentum equation was tested by Compton in an experiment where photons were observed to be scattered at all angles by electrons of the scattering material. So, the electromagnetic radiation has both the particle and wave aspects. If the radiation can be treated as waves as well as particles then how do the real particles behave? One should expect that the behaviour of real particles must be capable of description in terms of waves. In 1924, de Broglie combined the ideas of Planck (Eq. 1.2) and Einstein (Eq. 1.3) into a relationship between mass and frequency.

$$mc^2 = h\nu \tag{1.5}$$

Hence, the relationship between velocity v, and momentum p, becomes

$$p = mv = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{1.6}$$

Thus, it was possible to associate waves with every moving particle in nature. This relation should hold also for heavier particles which we are able to see. But, on account of heavier mass, λ becomes so small that there is a great difficulty in discovering the wave phenomenon associated with heavier particles. This concept of the wave-particle duality of matter was subjected to experimental test by Davisson and Germer in 1927 and independently by Thompson in 1928 who showed that a beam of electrons did indeed behave as if it were waves and underwent diffraction from a suitable grating.

1.2 Wave Equation

If electrons have the wave properties then there must be a wave equation and a wave function to describe the electron waves just as the waves of light, sound and strings are described. Let us consider the motion of a string which is held fixed at two ends $x = 0$ and $x = a$. It is possible to excite with care certain kinds of vibrations in which all points of the string move so that their displacements vary with time in the same way and all points are at their maximum displacements at the same time and have their maximum velocity at the same time. If the displacement occurs in the y-direction, mathematically these motions can be described by functions of the form

$$y(x, t) = f(x)\phi(t) \tag{1.7}$$

where $f(x)$ is independent of t and $\phi(t)$ is independent of x. Such motions are called normal modes of vibration. The wave equation has the general form

$$\frac{d^2y}{dx^2} = \frac{1}{c^2}\frac{d^2y}{dt^2} \tag{1.8}$$

where c is called the wave velocity. Substituting for y from Eq. (1.7) in Eq. (1.8) one obtains

$$\frac{c^2}{f(x)}\frac{d^2f(x)}{dx^2} = \frac{1}{\phi(t)}\frac{d^2\phi(t)}{dt^2} = -\omega^2 \tag{1.9}$$

In Eq. (1.9) the variables are separated and they may be equated to the same constant, say $-\omega^2$. This gives us two ordinary differential equations

$$\frac{d^2\phi(t)}{dt^2} + \omega^2\phi(t) = 0 \tag{1.10}$$

$$\frac{d^2f(x)}{dx^2} + \frac{\omega^2 f(x)}{c^2} = 0 \tag{1.11}$$

(For solutions of the second order differential equations of this form, see Appendix 1).

Equation (1.10) has the solution

$$\phi(t) = A \sin \omega t + B \cos \omega t \tag{1.12}$$

where the two constants A and B are determined from the boundary conditions, and ω is called the circular frequency which is related to the ordinary frequency ν as

$$\omega = 2\pi\nu \tag{1.13}$$

Equation (1.11) may therefore be written as

$$\frac{d^2f(x)}{dx^2} + \frac{4\pi^2\nu^2}{c^2}f(x) = 0 \tag{1.14}$$

Setting $\lambda = c/\nu$, the general solution of Eq. (1.14) may be written as

$$f(x) = A_1 \exp\left(+\frac{i2\pi x}{\lambda}\right) + A_2 \exp\left(-\frac{i2\pi x}{\lambda}\right) \tag{1.15}$$

or as (see Appendix 1)

$$f(x) = C \sin \frac{2\pi}{\lambda}x + D \cos \frac{2\pi}{\lambda}x \tag{1.16}$$

where A_1, A_2, C, and D are constants. Let us consider Eq. (1.16) and impose the boundary conditions

(i) $f(x) = 0$ at $x = 0$; and
(ii) $f(x) = 0$ at $x = a$

where a is the length of the string. From the boundary condition (i), $D = 0$ and from the condition (ii),

$$C \sin \frac{2\pi}{\lambda}a = 0$$

or

$$\sin \frac{2\pi a}{\lambda} = 0$$

or

$$\frac{2a}{\lambda} = n, \quad n = 1, 2, 3, \ldots \tag{1.17}$$

where n is a positive integer. Thus

$$a = n\frac{\lambda}{2} \tag{1.18}$$

The normal modes are thus the stationary sine waves given by

$$f(x) = C \sin \frac{n\pi}{a}x \tag{1.19}$$

and the wavelengths λ are such that the length of the string is an integral number of half waves. The complete solution for a normal mode in a stretched string therefore follows from Eqs. (1.17), (1.12), (1.13) and (1.19), and is given by

$$y(x, t) = C \sin \frac{n\pi}{a} x \cdot (A \sin 2\pi\nu t + B \cos 2\pi\nu t) \tag{1.20}$$

Equation (1.20) is an expression for the amplitude of waves generated during the normal modes of vibration in a stretched string. The same equation should represent the amplitude of a de Broglie wave associated with a moving particle. We are, primarily concerned here, with the time-independent or stationary waves. Therefore, the equation for a standing sine wave of wavelength λ is given by

$$\psi = C \sin \frac{2\pi}{\lambda} x \tag{1.21}$$

where ψ, called the wave function, is the amplitude of the wave varying sinusoidally along x and C is the maximum amplitude. Double differentiation of Eq. (1.21) with resepect to x gives

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} C \sin \frac{2\pi}{\lambda} x = -\frac{4\pi^2}{\lambda^2} \psi \tag{1.22}$$

The kinetic energy T of a moving particle of mass m and velocity v is given by

$$T = \frac{1}{2} m v^2 = \frac{m^2 v^2}{2m} \tag{1.23}$$

Following the de Broglie relation [Eq. (1.6)], T becomes

$$T = \frac{h^2}{2m\lambda^2} \tag{1.24}$$

By using Eq. (1.22) to eliminate λ^2 from Eq. (1.24) we get

$$T = -\frac{h^2}{8\pi^2 m} \cdot \frac{1}{\psi} \frac{d^2\psi}{dx^2} \tag{1.25}$$

If the particle moves in a field whose potential energy is V, then

$$T = E - V = -\frac{h^2}{8\pi^2 m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} \tag{1.26}$$

where E is the total energy. This is Schrödinger's equation for a particle in one dimension. It is usually written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \tag{1.27}$$

In three dimensions this equation becomes:

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \tag{1.28}$$

1.3 Interpretation of ψ and Heisenberg's Uncertainty Principle

In classical mechanics the square of wave amplitude associated with electromagnetic radiation is interpreted as a measure of the radiation intensity. This suggests that we should make a similar association for de Broglie waves associated with electrons or any moving particle. Let the solution of the wave equation [Eq. (1.28)] be a function $\psi(x, y, z)$, called wave function. We may anticipate that some physically observable property of the electron is connected to $\psi^2(x, y, z)$ or more generally $\psi^*(x, y, z)$. $\psi(x, y, z)$ if ψ is a complex wave function[1]. For a system having electrons there are two ways in which $|\psi^2|$ or $|\psi^*\psi|$ can be interpreted. Either $|\psi^2|$ may be regarded as a measure of the density of electrons or $|\psi^2|\,dr$ be interpreted as a measure of probability of finding the electrons in a small volume dr[2] in a certain region of space. The Born interpretation of ψ is that $|\psi^*\psi|\,dr$ or $|\psi^2|\,dr$ is proportional to the probability of finding the electrons in an infinitesimal region between r and $r + dr$. This implies that even if we know ψ exactly we cannot say precisely where the electrons can be found. This destroys the classical concept of a precise trajectory.

Let us consider an electron of mass m_e with momentum p_x moving in a zero potential field along the x-direction only. The wave equation for such particle according to our discussion in (Sec. 1.2) is given by

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2} p_x^2 \cdot \psi = 0 \tag{1.29}$$

Set $k^2 = \dfrac{4\pi^2 p_x^2}{h^2}$, then one writes

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{1.30}$$

The wave function $\psi(x)$ is given by either $\exp(ikx)$ or $\exp(-ikx)$ [see Appendix 1]. We now ask whether the electron whose momentum is p_x can be found. The answer is given by

$$|\psi^*(x)\,\psi(x)|$$

which can be written as

$$\psi^*(x)\psi(x) = \exp(-ikx)\exp(ikx) = 1 \tag{1.31}$$

According to Born interpretation, this result implies that the probability of finding the electron in a region dx is the same wherever dx is situated. Thus quantum mechanics says that if any part of the space is inspected, probability of finding the electron remains the same. In other words, if the momentum of a moving particle is precisely known, its position is totally uncertain.

In 1927 Heisenberg derived a famous principle known as uncertainty principle which is the most fundamental point on which the conclusions of

---

1. If $\psi = a + ib$ where $i = \sqrt{-1}$, then $\psi^* = a - ib$, so that $\psi^*\psi = a^2 + b^2$, a real function.
2. $dr = dx\,dy\,dz$

quantum mechanics or wave mechanics diverge from those of classical mechanics. In classical mechanics one can simultaneously determine as many properties of a system of any particle as one wishes, to any degree of accuracy. This is not true in wave mechanics.

Suppose a tiny particle is at rest. We want to find its exact position by looking through a microscope. To see a particle we must hit the particle with photons. If the light has a wavelength λ, we cannot expect to determine the position within a distance shorter than λ because of diffraction. So λ is the order of the uncertainty in the measurement of position. But a photon of wave length λ has a momentum $|h/\lambda|$. When a photon collides a particle it transfers this much momentum to the particle and the uncertainty in momentum is $|h/\lambda|$. The product of the uncertainties of the position and momentum is $\lambda(h/\lambda) = h$.

According to more accurate treatment of Heisenberg, his principle states that if the momentum is known to lie within a range Δp_x along, say, the x-axis then the position of the particle on this axis must be uncertain to an extent of Δx where

$$\Delta p_x \cdot \Delta x \geqslant \frac{h}{4\pi} \tag{1.32}$$

Under such circumstances the best thing one can do is to accept the Born interpretation of the wave function. For this reason $|\psi^2|$ or $|\psi^*\psi|$ may be called the probability function. Since the electron must be somewhere in space, the integration of $|\psi^2|$ or $|\psi^*\psi|$ over all space must be unity, so that

$$\int \psi^*(r)\psi(r)\, dr = 1 \tag{1.33}$$

Such wave functions are said to be normalised. For every system which is bound, every wave function must satisfy Eq. (1.33).

1.4 Properties of ψ

A second-order differential equation like [Eq. (1.28)] may give rise to several solutions though not necessarily all of them correspond to any physical or chemical reality. Such wave functions are therefore considered unacceptable. Acceptable wave functions are those which satisfy the following conditions:

1. ψ is single valued, i.e. for each value of the variables x, y, z, there is only one value of the function ψ. If one of the variables is an angle, say θ, then it requires that
$$\psi(\theta) = \psi(\theta + 2n\pi)$$
where n is an integer.
2. ψ and its first derivative with respect to its variables are continuous. In other words, there must not exist any sudden changes in ψ as its variables are changed.
3. For bound states ψ must vanish at infinity. If ψ be a complex function, then $\psi^*\psi$ must vanish at infinity.

If the above three conditions are satisfied the function ψ is called a well-behaved function.

APPENDIX 1

In this appendix we will show how a simple differential equation of the second order of the following form

$$\frac{d^2y}{dx^2} + k^2y = 0 \tag{A1.1}$$

can be solved. In Eq. (A1.1) k^2 is constant. Such an equation is satisfied by a function of an exponential form. Let us assume the solution of Eq. (A1.1) as

$$y = \exp(mx) \tag{A1.2}$$

Then substituting for y, $\exp(mx)$ in Eq. (A1.1), we obtain the auxiliary equation

$$m^2 + k^2 = 0 \tag{A1.3}$$

The roots of Eq. (A1.3) are given by

$$m = \pm ik \tag{A1.4}$$

where $i = \sqrt{-1}$. The particular solutions of Eq. (A1.1) are $\exp(+ikx)$ and $\exp(-ikx)$. On adding these particular solutions there results a solution with two independent arbitrary constants and therefore the complete solution of Eq. (A1.1) is written as

$$y = A_1 \exp(ikx) + A_2 \exp(-ikx) \tag{A1.5}$$

On expanding the exponentials in sines and cosines we obtain the following equivalent form

$$\begin{aligned} y &= A_1(\cos kx + i \sin kx) + A_2(\cos kx - i \sin kx) \\ &= (A_1 + A_2)\cos kx + (A_1 - A_2)\, i \sin kx \\ &= C \cos kx + D \sin kx \end{aligned} \tag{A1.6}$$

In Eqs. (A1.5) and (A1.6), A_1, A_2, C and D are arbitrary constants.

PROBLEMS

1. An electron moves in an electric field with kinetic energy of 2.5 eV. What is its associated de Broglie wavelength?
2. Find the energy jump in electron volts for the emission of visible light of wavelength 7500 Å.
3. Show that as x increases by λ in the wave

   $$\psi = A \exp\left(\frac{2\pi i x}{\lambda}\right)$$

   the amplitude, ψ goes through one cycle.
4. When x-rays of wavelength 1.5 Å are allowed to hit an atom they eject an inner electron which moves after collision with the velocity of 2.14×10^9 cm/s. Find the binding energy of that electron in the atom.

2

Operator Concept in Quantum Chemistry

2.1 Operators

We have learnt in the previous chapter that wave function describes the state of a system so that any observable quantity can be derived from it. The mathematical process for carrying out the derivation involves the concept of operators. *To every physically measurable or observable quantity like position, velocity, linear momentum, angular momentum, energy, etc. of a system there corresponds an operator in quantum mechanics.* This may be treated as one of the several basic postulates of quantum mechanics.

An operator is a symbol for a certain mathematical procedure which transforms one function into another. For example, the operator of evaluating the derivative with respect to x is represented by the symbol d/dx. When this operator is applied to the function x^n we obtain a new function as

$$\frac{d}{dx}(x^n) = nx^{n-1}$$

A list of typical examples of different mathematical operations along with the results of the operations on the function, x^3 is given in Table 1.

TABLE 1

Operation	*Operator*	*Result of operation on x^3*
Taking the square	$(\ )^2$	x^6
Taking the square root	$\sqrt{\ }$	$x^{3/2}$
Multiplication by a constant k	k	kx^3
Differentiation with respect to x	$\frac{d}{dx}$	$3x^2$
Integration with respect to x	$\int (\ )\, dx$	$x^4/4 + c$

Evidently, an operator is a set of instructions embodied in the definition of the operator and the operations can always be written in the form of an equation

$$(\text{Operator})\cdot(\text{function}) = (\text{Another function}) \qquad (2.1)$$

The function on which the operation is carried out is often called an operand. The left hand side of Eq. (2.1) does not mean that the function is multiplied by the operator. In a sense an operator therefore does not have any meaning when it stands alone. However, it is possible to formulate an algebra of operators with operators in a manner analogous to the manipulation of numbers in ordinary algebra. An operator, unless it is otherwise obvious, is hereafter written with a symbol (^) overhead.

Addition and Subtraction of Operators

New operators can be constructed by adding and subtracting operators. If $\hat{A}$ and $\hat{B}$ are two different operators, then new operators $\widehat{A+B}$ and $\widehat{A-B}$ can be defined as

$$\left.\begin{aligned} (\widehat{A+B})f &= \hat{A}f + \hat{B}f \\ (\widehat{A-B})f &= \hat{A}f - \hat{B}f \end{aligned}\right\} \tag{2.2}$$

where f is an operand.
It is also true that

$$\left.\begin{aligned} \widehat{A+B} &= \hat{B} + \hat{A} \\ \widehat{A-B} &= -\hat{B} + \hat{A} \end{aligned}\right\} \tag{2.3}$$

Multiplication of Operators

The consecutive operations with two or more operators on a function may be called the multiplication of operators. Let $\hat{A}$ and $\hat{B}$ represent two different operators and f, an operand. Then, the expression $\hat{A}\hat{B}f$ means that the function f is first operated on with $\hat{B}$ to obtain a new function, f' as

$$\hat{B}f = f'$$

Then f' is operated on by $\hat{A}$ to obtain the final function f'' as

$$\hat{A}f' = f''$$

so that

$$\hat{A}\hat{B}f = f''$$

The order of application of operators is always from right to left as they are written.
If the same operator is applied several times in succession, it is written with a power. Thus

$$\hat{A}\hat{A}f = \hat{A}^2f$$

Let us suppose that the operator $\hat{A}$ stands for taking the derivative with respect to x and the operator $\hat{B}$ for the multiplication by x. Then

$$\hat{A}\hat{B}f(x) = \hat{A}[\hat{B}f(x)] = \hat{A}[Xf(x)] = X\frac{df(x)}{dx} + f(x)$$

$$\hat{B}\hat{A}f(x) = \hat{B}[\hat{A}f(x)] = \hat{B}\left[\frac{df(x)}{dx}\right] = X\frac{df(x)}{dx}$$

Therefore

$$\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x) \tag{2.4}$$

This shows that the result of a series of operations is often different depending on the sequence in which the operations are performed. If the result of two operations is same regardless of the sequence in which the operations are performed, the two operators are said to commute. The above two operators $\hat{A}$ and $\hat{B}$ do not commute. This distinguishes an operator algebra from the ordinary algebra where for any two numbers a and b

$$a \times b = b \times a$$

Linear Operator

If in operating on the sum of two functions an operator gives the same result as the sum of the operations on the two functions separately, then the operator is said to be linear. Thus the operator $\hat{A}$ is linear if for any functions f and g we have

$$\hat{A}(f + g) = \hat{A}f + \hat{A}g \tag{2.5}$$

and $\hat{A}cf = c\hat{A}f$ where c is a constant.
The operation of taking square root is non-linear because

$$\sqrt{f + g} \neq \sqrt{f} + \sqrt{g} \tag{2.6}$$

Commutator

Using any two operators $\hat{A}$ and $\hat{B}$, it is possible to construct a new operator $(A\widehat{B - B}A)$, called commutator of the two operators $\hat{A}$ and $\hat{B}$ usually written as $[A, B]$. If these two operators commute then

$$[A, B] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

and therefore, this commutator means the multiplication with zero. Clearly, every operator commutes with itself or any power of it. Thus, for an operator $\hat{A}$

$$\hat{A}\hat{A}^n - \hat{A}^n\hat{A} = 0 \tag{2.7}$$

On the other hand, the operators (d/dx) and the multiplication by x, written as $\hat{X}$ do not commute as shown earlier in Eq. (2.4). We may write the commutator of the operators (d/dx) and $\hat{X}$ as

$$\left(\frac{d}{dx}\right)(\hat{X}) - (\hat{X})\left(\frac{d}{dx}\right) = \left[\frac{d}{dx}, X\right] = 1$$

In other words, this commutator is an unit operator.

Vector Operator

Operators are not necessarily limited to operate on functions of one variable. The differential operator ∂/∂_x can operate on the function $f(x, y, z)$. An important group of operators are the vector operators. A vector operator ∇ ('del') is defined in Cartesian coordinates as

$$\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z} \tag{2.8}$$

where i, j, k, are unit vectors along the x, y and z axes. Operating on a scalar function ϕ, this operator generates a vector called the gradient of ϕ.

$$\nabla\phi = i\frac{\partial\phi}{\partial x} + j\frac{\partial\phi}{\partial y} + k\frac{\partial\phi}{\partial z} \tag{2.9}$$

Laplacian

Of particular interest in quantum mechanics is the Laplacian operator ∇^2 defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2.10}$$

Eigenfunctions and Eigenvalues

Since ∇^2 is an important operator used in quantum mechanics we shall study the behaviour of such an operator in more detail. Consider the following expression

$$\frac{\partial^2\psi}{\partial x^2} = -\lambda\psi \tag{2.11}$$

where λ is independent of x. This is a simple second-order differential equation.

The general solution of Eq. (2.11) may be written either as

$$\psi = A_1 \exp(i\sqrt{\lambda}\cdot x) + A_2 \exp(-i\sqrt{\lambda}\cdot x) \tag{2.12}$$

where A_1 and A_2 are two arbitrary constants, or as (see Appendix 1)

$$\psi = C\cdot\cos\sqrt{\lambda}\cdot x + D\cdot\sin\sqrt{\lambda}\cdot x \tag{2.13}$$

For $\lambda > 0$, $\sqrt{\lambda}$ is a non-vanishing positive number, and the general solution given by Eq. (2.13) is well-behaved, since it is continuous, single valued and never increases to infinity because the magnitude of sin θ or cos θ always oscillates from $+1$ to -1.

For $\lambda < 0$, $\sqrt{\lambda}$ is a non-vanishing imaginary number. Let, $\sqrt{\lambda} = ia$, where a is a real positive number. Then ψ of Eq. (2.12) may be written as

$$\psi = A_1 \exp(-ax) + A_2 \exp(ax) \tag{2.14}$$

This function is single valued and continuous but increases to infinity at $x = \pm\infty$. Such a function is not well-behaved.

For $\lambda = 0$, Eq. (2.11) becomes

$$\frac{\partial^2\psi}{\partial x^2} = 0 \tag{2.15}$$

and therefore,

$$\psi = Ax + B \tag{2.16}$$

where A and B are two arbitrary constants. The function ψ of Eq. (2.16) cannot be well-behaved because it increases to infinity at $x = \pm\infty$. Since A and B are two arbitrary constants, we may assume $A = 0$, then $\psi = B$ which is again a well-behaved function.

Thus we have seen that for $\lambda > 0$, the general solution of Eq. (2.11) is well-behaved and for $\lambda = 0$ a particular solution is well-behaved while for $\lambda < 0$ there is no well-behaved solution. If, for certain values of λ, the operand ψ is well-behaved, then λ is called the eigenvalue (or characteristic value) and ψ; the eigenfunction of the operator [in Eq. (2.11) the operator is $-\partial^2/\partial x^2$].

2.2 Second Postulate of Quantum Mechanics

According to another basic postulate or law of quantum mechanics, *the only possible values that can be observed of a physical property like angular momentum, energy, etc. of a system are the eigenvalues* λ, *in the operator equation*:

$$\hat{A}\psi = \lambda\psi \tag{2.17}$$

where $\hat{A}$ *is the operator for the physical quantity and* ψ *is the well-behaved eigenfunction.* However, we shall see later, that the form of operators for various physical quantities can be derived from the direct physical considerations and then by solving the above Eq. (2.17), the eigenvalues and eigenfunctions can be found.

Since the observable physical quantities have obviously real magnitude, the eigenvalues, λ of Eq. (2.17) must be real.

Hermitian and Unitary Operators

There are two types of operators which obey the eigenvalue equation (2.17).

They are the hermitian and unitary operators. An operator $\hat{A}$ is said to be hermitian if

$$\int \psi_1^* \cdot (\hat{A}\psi_2)\partial\tau = \int (\hat{A}\psi_1)^* \cdot \psi_2 \partial\tau \tag{2.18}$$

where ψ_1 and ψ_2 are two eigenfunctions of the operator $\hat{A}$. This is known as the 'Turn-over rule'. The asterisk as superscript indicates the complex conjugate of the quantity immediately to its left. Hermitian operator is linear and has real eigenvalues. If $\hat{A}$ is a hermitian operator and ψ, an eigenfunction with eigenvalue a, then

$$\hat{A}\psi = a \cdot \psi \tag{2.19}$$

Multiplying both sides of the equation with ψ^* and integrating over all space we get

$$\int \psi^* \cdot \hat{A}\psi\partial\tau = a\int \psi^*\psi\partial\tau \tag{2.20}$$

Taking the complex conjugate of every quantity in Eq. (2.19),

$$\hat{A}^*\psi^* = a^* \cdot \psi^* \tag{2.21}$$

and then multiplying both sides with ψ and integrating, one gets

$$\int \psi \cdot \hat{A}^*\psi^*\partial\tau = a^*\int \psi^*\psi\partial\tau \tag{2.22}$$

The left hand side of Eqs. (2.20) and (2.22) are equal according to the definition of a hermitian operator, so that

$$a\int \psi^*\psi\partial\tau = a^*\int \psi^*\psi\partial\tau \tag{2.23}$$

In other words, $a = a^*$, which is true only if a is real. This guarantees that any physical quantity (often called dynamical variable) represented by a hermitian operator is observable and physically measurable.

A unitary operator $\hat{U}$ is also a linear operator and defined as

$$\int \psi_1^* \cdot \hat{U}^{-1}\psi_2\partial\tau = \int \psi_2\hat{U}^*\psi_1^*\partial\tau \tag{2.24}$$

where the operator $\hat{U}^{-1}$ is the inverse of $\hat{U}$, such that $\hat{U}^{-1}\hat{U} = \hat{U}\hat{U}^{-1}$ and ψ_1 and ψ_2 are any two eigenfunctions of $\hat{U}$ and the asterisk stands for the complex conjugate quantity. Consider the equation

$$\hat{U}\psi = \lambda \cdot \psi \tag{2.25}$$

where λ is the eigenvalue. Then

$$\hat{U}^{-1}\hat{U}\psi = \psi = \lambda \cdot \hat{U}^{-1}\psi$$

or
$$\hat{U}^{-1}\psi = \lambda^{-1}\cdot\psi \tag{2.26}$$

Inverse operator $\hat{U}^{-1}$ has the same eigenfunction as $\hat{U}$ but with reciprocal eigenvalue. Multiplying both sides of Eq. (2.26) with ψ^* and integrating over all space one gets

$$\int \psi^*\cdot\hat{U}^{-1}\psi\partial\tau = \lambda^{-1}\cdot\int\psi^*\psi\partial\tau \tag{2.27}$$

Taking the complex conjugate of Eq. (2.25)

$$\hat{U}^*\psi^* = \lambda^*\cdot\psi^* \tag{2.28}$$

Then

$$\int \psi\cdot\hat{U}^*\psi^*\partial\tau = \lambda^*\int\psi^*\psi\partial\tau \tag{2.29}$$

Following the definition of unitary operator, the right hand sides of Eqs. (2.27) and (2.29) are equal, so that

$$\lambda^{-1} = \lambda^* \tag{2.30}$$

or
$$\lambda^*\cdot\lambda = 1 \tag{2.31}$$

Thus eigenvalues of an unitary operator have modulus one.

2.3 Setting up of Operators for Different Observables

It has been already mentioned that every dynamical variable is assigned a linear operator. According to classical mechanics, most dynamical variables may be expressed in terms of the position and momentum coordinates such as x, y, z, p_x, p_y, or p_z. The rule for setting up their quantum mechanical operators is simply to take the classical expressions and replace x, y, z, p_x, p_y and p_z, by the corresponding operators. Operators corresponding to positions along x, y and z axes are simply the multiplication by the variable itself. Operators for linear momenta may be found from the following considerations.

A beam of electrons travelling along the x-direction can be treated as a wave propagating along the x-axis. Taking these waves to be sinusoidal, the wavefunction may be written as

$$\psi = A\sin\frac{2\pi x}{\lambda} \tag{2.32}$$

where λ is the wavelength. An equivalent form for the time-independent wave is

$$\psi = C\cdot\exp\left(\pm 2\pi i\frac{x}{\lambda}\right) \tag{2.33}$$

Then
$$\frac{\partial\psi}{\partial x} = \pm\frac{2\pi i}{\lambda}C\exp\left(\pm\frac{2\pi i}{\lambda}x\right) \tag{2.34}$$
$$= \pm\frac{2\pi i}{\lambda}\psi$$

Using de Broglie's relationship, i.e. $\lambda = h/P_x$, one may write

$$\hat{P}_x\psi = \pm\frac{h}{2\pi i}\frac{\partial\psi}{\partial x} \tag{2.35}$$

Therefore, the operator corresponding to the linear momentum in the x-direction is written as

$$\hat{P}_x = \frac{h}{2\pi i}\frac{\partial}{\partial x} \quad \text{and} \quad \hat{P}_x^* = -\frac{h}{2\pi i}\frac{\partial}{\partial x} \tag{2.36}$$

Similarly for $\hat{P}_y$ and $\hat{P}_z$ one can write

$$\hat{P}_y = \frac{h}{2\pi i}\frac{\partial}{\partial y}, \qquad \hat{P}_z^* = \frac{-h}{2\pi i}\frac{\partial}{\partial z} \tag{2.37}$$

That the operator, say p_x, is hermitian is shown as follows

$$\int_{-\infty}^{\infty} \psi_1^*\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)\psi_2\,dx = \frac{h}{2\pi i}\Big[\psi_1^*\psi_2\Big]_{-\infty}^{+\infty} - \frac{h}{2\pi i}\int_{-\infty}^{\infty}\psi_2\frac{\partial\psi_1^*}{\partial x}\,dx$$

The first term on the right hand side is zero since both ψ_1 and ψ_2 vanish at infinity. The second term on the right hand side can be written as

$$\int_{-\infty}^{\infty}\psi_2\cdot\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^*\psi_1^*\,dx$$

Thus, the linear momentum operator is hermitian, hence linear momentum is observable.

The classical expression for the total energy of a single particle of mass m is called the hamiltonian, usually denoted by H and is given by

$$\begin{aligned} H &= \frac{1}{2}mv^2 + V \\ &= \frac{m^2v^2}{2m} + V \\ &= \frac{p^2}{2m} + V \end{aligned} \tag{2.38}$$

where v is the linear velocity, p the momentum, and V the potential energy of the particle. Written in terms of the components of the linear momentum p, H becomes

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V \tag{2.39}$$

The operator, say $\hat{P}_x^2$, is taken to mean that the corresponding operation P_x is to be repeated twice, so that

$$\begin{aligned} \hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2 = {} & \left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right) + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)\left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right) \\ & + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)\left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right) \end{aligned}$$

$$= -\frac{h^2}{4\pi^2}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

$$= -\frac{h^2}{4\pi^2}\nabla^2 \tag{2.40}$$

Substituting Eq. (2.40) in Eq. (2.39)

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \tag{2.41}$$

which can be proved to be hermitian and linear. If there are several particles then

$$H = -\frac{h^2}{8\pi^2}\sum_i \frac{\nabla_i^2}{m_i} + V \tag{2.42}$$

where m_i is the mass of the i^{th} particle and ∇_i^2 is the Laplacian operator containing the coordinates of i^{th} particle.

Another important dynamical variable is the angular momentum. For a single particle moving around a fixed point, the angular momentum $\boldsymbol{L}$ is given by the vector product of $\boldsymbol{r}$ and $\boldsymbol{p}$ as

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \tag{2.43}$$

where $\boldsymbol{r}$ is the radius vector from a fixed point and $\boldsymbol{p}$, the linear momentum vector. Both the vectors $\boldsymbol{r}$ and $\boldsymbol{p}$ can be written in terms of their components as

$$\begin{aligned} \boldsymbol{r} &= \boldsymbol{i}x + \boldsymbol{j}y + \boldsymbol{k}z \\ \boldsymbol{p} &= \boldsymbol{i}p_x + \boldsymbol{j}p_y + \boldsymbol{k}p_z \end{aligned} \tag{2.44}$$

where $\boldsymbol{i}, \boldsymbol{j}$ and $\boldsymbol{k}$ are unit vectors along x, y and z axes. Therefore, in terms of the components of $\boldsymbol{r}$ and $\boldsymbol{p}$, the angular momentum, $\boldsymbol{L}$ is

$$\boldsymbol{L} = \boldsymbol{i}(yp_z - zp_y) + \boldsymbol{j}(zp_x - xp_z) + \boldsymbol{k}(xp_y - yp_x) \tag{2.45}$$

Replacing the p's by the corresponding quantum mechanical operators, the operators for the components of angular momentum are as follows:

$$\left.\begin{aligned} \hat{L}_x &= \frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y &= \frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z &= \frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right\} \tag{2.46}$$

The total angular momentum is obviously given by

$$\boldsymbol{L} = \boldsymbol{i}L_x + \boldsymbol{j}L_y + \boldsymbol{k}L_z \tag{2.47}$$

However, more important in quantum mechanics, is the scalar product of $\boldsymbol{L}$ with itself,

$$\boldsymbol{L}\cdot\boldsymbol{L} = L^2 = L_x^2 + L_y^2 + L_z^2 \tag{2.48}$$

The angular momentum operators are usually expressed in spherical polar coordinates. By means of transformations shown in Appendix 2, we find

$$\left.\begin{aligned} \hat{L}_x &= \frac{h}{2\pi i}\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right] \\ \hat{L}_y &= \frac{h}{2\pi i}\left[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right] \\ \hat{L}_z &= \frac{h}{2\pi i}\frac{\partial}{\partial\phi} \end{aligned}\right\} \tag{2.49}$$

$$\hat{L}^2 = -\frac{h^2}{4\pi^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi}\right]$$

Let us consider the component of angular momentum about z-axis, i.e. $\hat{L}_z$. That this operator is hermitian can be shown as follows

$$\int_0^{2\pi}\psi_2^*\left(\frac{h}{2\pi i}\frac{\partial}{\partial\phi}\right)\psi_1\,d\phi = \frac{h}{2\pi i}\left\{\left[\psi_2^*\psi_1\right]_0^{2\pi} - \int_0^{2\pi}\psi_1\frac{\partial\psi_2^*}{\partial\phi}d\phi\right\} \tag{2.50}$$

Since the functions $\psi_1(\phi)$ and $\psi_2(\phi)$ must be single valued i.e. for any ϕ,

$$\psi(\phi) = \psi(2\pi + \phi) \tag{2.51}$$

the first term on the right hand side of Eq. (2.50) must vanish. Therefore, Eq. (2.50) can be written as

$$\int_0^{2\pi}\psi_2^*\cdot\left(\frac{h}{2\pi i}\frac{\partial}{\partial\phi}\right)\psi_1\,d\phi$$

$$= -\frac{h}{2\pi i}\int_0^{2\pi}\psi_1\frac{\partial\psi_2^*}{\partial\phi}d\phi = \int_0^{2\pi}\psi_1\left(\frac{h}{2\pi i}\frac{\partial}{\partial\phi}\right)^*\psi_2^*\,d\phi \tag{2.52}$$

Because of the equivalence of $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$, an operator corresponding to any component of angular momentum is hermitian. So $\hat{L}^2$ must also be hermitian. This shows that not only any component of angular momentum about any axis but also total angular momentum in a system is observable from the quantum mechanical view point.

Eigenvalues of $\hat{L}_z$

In accordance with the basic postulate embodied in Eq. (2.17), the possible values of the component of angular momentum about z-axis, the axis of rotation, are given by the solutions of equation

$$\hat{L}_z\psi = \lambda\psi \tag{2.53}$$

or

$$\frac{\partial\psi}{\partial\phi} = \frac{2\pi i}{h}\lambda\cdot\psi$$

or

$$\psi = \exp\left(\frac{2\pi i}{h}\lambda\phi\right) = \cos\left(\frac{2\pi\lambda}{h}\phi\right) + i\sin\left(\frac{2\pi\lambda}{h}\phi\right) \tag{2.54}$$

Since the function ψ must be single valued, it follows from Eq. (2.51) that

$$\exp\left(\frac{2\pi i\lambda}{h}\phi\right) = \exp\left(\frac{2\pi i\lambda}{h}[\phi + 2\pi]\right)$$

$$\exp(ik\phi) = \exp(ik[\phi + 2\pi]) \tag{2.55}$$

where
$$k = \frac{2\pi}{h}\lambda$$

or
$$\exp(2\pi ik) = 1 \tag{2.56}$$

In other words,

$$\cos(2\pi k) + i\sin(2\pi k) = 1 \tag{2.57}$$

which is possible only if

$$k = 0, \pm 1, \pm 2, \pm 3 \ldots \pm n \tag{2.58}$$

Or, λ must be either zero or integral multiple of $h/2\pi$. This result is exactly what Bohr postulated about angular momentum of an electron in an atom. In other words, the component of angular momentum about any axis forms a discrete eigenspectrum. On the other hand, it can be shown that in the absence of any restrictions, the component of linear momentum along any axis forms a continuous eigenspectrum. (See answer to Problem 2 of this chapter.)

2.4 Third Postulate of Quantum Mechanics

In accordance with the second postulate given by Eq. (2.17), the eigenvalue λ, which a measurement of an observable characterised by an operator $\hat{A}$ leads to, ought to be written as

$$\lambda = \frac{\hat{A}\psi}{\psi} \tag{2.59}$$

But this form of expression is not used in quantum mechanics, because the expression $\hat{A}\psi/\psi$ will be a function of the coordinates of the system and as such it varies from place to place and cannot be equated to a constant λ. If, however, both the numerator and the denominator on the right hand side of Eq. (2.59) are multiplied with ψ^* and integrated over the entire space accessible to the system then the expression $\int \psi^*\hat{A}\psi\partial\tau / \int \psi^*\psi\partial\tau$ no longer becomes a function of the coordinates and can then appropriately be equated to an average value of the constant λ. The third postulate may then be stated as follows:

When a great many measurements of any observable represented by an operator $\hat{A}$ are made on a system characterised by a function ψ, the average result obtained is given by

$$\bar{\lambda} = \frac{\int \psi^* \hat{A} \psi \partial\tau}{\int \psi^* \psi \partial\tau} \tag{2.60}$$

The bar over λ is used to indicate the average result.

2.5 Fourth Postulate of Quantum Mechanics

In this section we shall briefly discuss the question of the time evolution of a quantum mechanical system. If the wave function ψ of a physical system is given at a certain instant, not only all the properties of the system at that instant are described but its behaviour at all subsequent instants is also determined. The mathematical expression of this fact is that $(\partial\psi/\partial t)$ (derivative of the wave function with respect to time) at any given instant must be determined by the value of the function itself at that instant. Thus, the fourth postulate may be stated as follows:

The time development of a wave function is given by

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \hat{H}\psi \tag{2.61}$$

which is Schrodinger's equation where H is the hamiltonian operator.

If we substitute for $\hat{H}$ from Eq. (2.41) in Eq. (2.61), we have

$$\left[-\frac{h^2}{8\pi^2 m}\nabla^2 + V(r)\right]\psi = \frac{ih}{2\pi}\frac{\partial\psi}{\partial t} \tag{2.62}$$

The wave function ψ in Eq. (2.62) is obviously a function of the space coordinates of a particle, i.e. x, y, z and time t. Using a collective symbol r for the space coordinates x, y, z, one can write Eq. (2.62) as

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial r^2} + V(r)\psi = \frac{ih}{2\pi}\frac{\partial\psi}{\partial t} \tag{2.63}$$

We have supposed that the potential V is independent of time. Such an equation can be solved easily by assuming the separation of variables. Thus, the wave function ψ may be factorised into two functions, one depending only on r and the other on t. One may try the following:

$$\psi(r, t) = \psi(r)\psi'(t) \tag{2.64}$$

or

$$\frac{\partial\psi(r, t)}{\partial r} = \psi'(t)\frac{\partial\psi(r)}{\partial r}$$

or

$$\frac{\partial^2\psi(r, t)}{\partial r^2} = \psi'(t)\frac{\partial^2\psi(r)}{\partial r^2} \tag{2.65}$$

Similarly

$$\frac{\partial\psi(r, t)}{\partial t} = \psi(r)\frac{\partial\psi'(t)}{\partial t} \tag{2.66}$$

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Using Eqs (2.65) and (2.66) in Eq. (2.63) one obtains

$$-\frac{h^2}{8\pi^2 m}\psi'(t)\frac{\partial^2\psi(r)}{\partial r^2}+V(r)\psi(r)\psi'(t)=\frac{ih}{2\pi}\psi(r)\frac{\partial\psi'(t)}{\partial t} \tag{2.67}$$

Dividing Eq. (2.67) by $\psi(r)\psi'(t)$ we have

$$\left\{-\frac{h^2}{8\pi^2 m}\frac{1}{\psi(r)}\frac{\partial^2\psi(r)}{\partial r^2}+V(r)\right\}=\frac{ih}{2\pi}\frac{1}{\psi'(t)}\frac{\partial\psi'(t)}{\partial t} \tag{2.68}$$

In Eq. (2.68), terms in the parentheses on the left hand side are independent of t while the term on the right hand side is independent of r. Thus the variables r and t are separated and each side of the Eq. (2.68) may be equated to a constant, say E, giving

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(r)}{\partial r^2}+V(r)\psi(r)=E\cdot\psi(r) \tag{2.69a}$$

and

$$\frac{ih}{2\pi}\frac{\partial\psi'(t)}{\partial t}=E\cdot\psi'(t) \tag{2.69b}$$

Suppose Eq. (2.69a) has the solution $\psi(r)$. Eq. (2.69b) has obviously the following solution

$$\psi'(t)=C\exp\left(-\frac{2\pi i}{h}E\cdot t\right) \tag{2.70}$$

So the wave function $\psi(r, t)$ may be written as

$$\psi(r,t)=\psi(r)\cdot C\cdot\exp\left[-\frac{2\pi i}{h}Et\right]$$

The constant C may be absorbed in $\psi(r)$, and we may write $\psi(r, t)$ as

$$\psi(r,t)=\psi(r)\cdot\exp\left[-\frac{2\pi i}{h}Et\right] \tag{2.71}$$

2.6 Derivative of an Operator with Respect to Time

The differentiation of an operator (hence the derivative of a physical quantity), with respect to time cannot be defined in quantum mechanics in the same way as in classical mechanics. In classical mechanics the derivative of any quantity with respect to time involves the consideration of the values of the quantity at two closely spaced intervals of time. In quantum mechanics, a quantity which has a definite value at a certain instant does not necessarily have definite value at other instants. It is therefore necessary to define the derivative of an operator with respect to time differently in quantum mechanics. The derivative of an operator $\hat{F}$ is usually defined as the quantity whose mean value is equal to the derivative, with respect to time, of the mean value of $\hat{F}$, i.e.

$$\overline{\frac{\partial\hat{F}}{\partial t}}=\frac{\partial\overline{\hat{F}}}{\partial t} \tag{2.72}$$

Since $$\bar{\hat{F}} = \int \psi^* \cdot \hat{F}\psi \partial\tau$$

where $$\int \psi^*\psi \partial\tau = 1$$

we have

$$\frac{\partial \bar{\hat{F}}}{\partial t} = \frac{\partial}{\partial t}\int \psi^* \cdot \bar{\hat{F}}\psi \partial\tau = \int \psi^* \frac{\partial \hat{F}}{\partial t}\psi \partial\tau + \int \frac{\partial \psi^*}{\partial t}\hat{F}\psi\partial\tau + \int \psi^* \cdot \hat{F}\frac{\partial \psi}{\partial \tau} d\tau \tag{2.73}$$

Here the operator $\hat{F}$ depends on time as a parameter. Substituting for $\partial\psi^*/\partial t$ and $\partial\psi/\partial t$ using Eq. (2.61), one gets

$$\frac{\partial \bar{\hat{F}}}{\partial t} = \int \psi^* \cdot \frac{\partial \hat{F}}{\partial t}\psi\partial\tau + \frac{2\pi i}{h}\int (\hat{H}^*\psi^*)\cdot \hat{F}\psi\partial\tau - \frac{2\pi i}{h}\int \psi^* \cdot \hat{F}(\hat{H}\psi)\partial\tau \tag{2.74}$$

Since the operator $\hat{H}$ is hermitian

$$\int (\hat{H}^*\psi^*)\cdot \hat{F}\psi\partial\tau = \int \psi^* \cdot \hat{H}\hat{F}\psi\partial\tau \tag{2.75}$$

Thus

$$\frac{\partial \bar{\hat{F}}}{\partial t} = \int \psi^* \frac{\partial \hat{F}}{\partial t}\psi\partial\tau + \frac{2\pi i}{h}\int \psi^* \cdot (\hat{H}\hat{F} - \hat{F}\hat{H})\psi\partial\tau \tag{2.76}$$

Combining Eqs (2.72) and (2.76) we have

$$\frac{\partial \bar{\hat{F}}}{\partial t} = \int \psi^* \left[\frac{\partial \hat{F}}{\partial t} + \frac{2\pi i}{h}(\hat{H}\hat{F} - \hat{F}\hat{H})\right]\psi d\tau \tag{2.77}$$

Eq. (2.77) leads to an interesting conclusion. If the operator $\hat{F}$ is explicitly independent of time and commutes with the hamiltonian $\hat{H}$, then $\hat{F}$ is a constant of the motion. In other words, the mean value of the quantity remains constant in time.

2.7 Some Important Theorems

2.7.1 If ψ_1 and ψ_2 be the eigenfunctions of a hermitian operator $\hat{A}$, with eigenvalues a_1 and a_2 respectively, then the eigenfunctions are orthogonal, i.e. $\int \psi_1^* \psi_2 \, d\tau = 0$

Hence, the integral $\int \psi_1^* \cdot \hat{A}\psi_2 d\tau$, often called the non-diagonal matrix element of the operator $\hat{A}$ vanishes.

Proof: By hypothesis

$$\hat{A}\psi_1 = a_1\psi_1 \tag{2.78}$$

$$\hat{A}\psi_2 = a_2\psi_2 \tag{2.79}$$

Take the complex conjugate of Eq. (2.78) and remember a_1 is real

$$\hat{A}^*\psi_1^* = a_1\psi_1^* \tag{2.80}$$

Multiply Eq. (2.80) with ψ_2 and integrate

$$\int \psi_2\hat{A}^*\psi_1^* d\tau = a_1\int \psi_2\psi_1^*\, d\tau \tag{2.81}$$

Likewise multiply Eq. (2.79) with ψ_1^* and integrate

$$\int \psi_1^*\hat{A}\psi_2\, d\tau = a_2\int \psi_1^*\psi_2\, d\tau \tag{2.82}$$

By definition of the hermitian operator, the left hand sides of Eqs. (2.81) and (2.82) are equal, thus

$$a_1\int\psi_1^*\psi_2\, d\tau = a_2\int\psi_1^*\psi_2\, d\tau$$

or

$$(a_1 - a_2)\int\psi_1^*\psi_2\, d\tau = 0 \tag{2.83}$$

Unless $a_1 = a_2$, the integral $\int\psi_1^*\psi_2\, d\tau$ must vanish. Hence the integrals appearing on the left hand sides of Eqs. (2.81) and (2.82) must also vanish.

If ψ_1 and ψ_2 have the same eigenvalue a, i.e. if the eigenfunctions are degenerate, then the two functions ψ_1 and ψ_2 may not be orthogonal. If $\hat{A}\psi_1 = a\psi_1$ and $\hat{A}\psi_2 = a\psi_2$ then any linear combination of ψ_1 and ψ_2 obeys the eigenvalue equation, i.e. $\hat{A}(\psi_1 + c\psi_2) = a(\psi_1 + c\psi_2)$ where c is a constant. However, it is possible to make the function $(\psi_1 + c\psi_2)$ orthogonal to ψ_1. Then, the requirement

$$\int\psi_1^*\cdot(\psi_1 + c\psi_2)\, d\tau = 0$$

gives

$$c = -\frac{\int \psi_1^*\psi_1\, d\tau}{\int \psi_1^*\psi_2\, d\tau} \tag{2.84}$$

This procedure can be repeated indefinitely as required by the degree of degeneracy of the eigenvalue a. This method of orthogonalisation is known as Schmidt orthogonalisation process.

2.7.2 If we have a set of eigenfunctions

$$\psi_1, \psi_2, \psi_3 \ldots$$

such that any two functions in the set are orthogonal, i.e.

$$\int \psi_i^* \psi_j \, d\tau = 0$$

and each function is normalised, i.e.

$$\int \psi_i^* \psi_i \, d\tau = 1$$

the set of functions is called orthonormal. The orthogonality and normalisation conditions can be conveniently combined in the expression

$$\int \psi_i^* \psi_j \, d\tau = \delta_{ij} \tag{2.85}$$

where δ_{ij}, is called Kronecker's delta, which is zero unless $j = i$, in which case it is unity. The great importance of the set of orthonormal functions lies in the possibility of expanding any arbitrary function in a series of these orthonormal functions. That is

$$\Phi = \sum_i c_i \psi_i \tag{2.86}$$

where the c_i's are constants. The function Φ is exact if the summation is taken over all the eigenfunctions which may constitute an infinite set. The proof of the statement has not been established in general but is found to be valid for the hermitian operators used in quantum mechanics. It will be shown later that this expansion method is the most common approach to getting approximate solutions of the Schrodinger equation.

2.7.3 If two operators $\hat{A}$ and $\hat{B}$ commute then they have the same set of eigenfunctions.

Proof: Suppose, the operator $\hat{A}$ has eigenfunction ψ_i, then

$$\hat{A}\psi_i = a_i \psi_i$$

where a_i is the eigenvalue. Since $\hat{A}$ and $\hat{B}$ commute

$$\hat{A}\hat{B}\psi_i = \hat{B}\hat{A}\psi_i = \hat{B}a_i\psi_i = a_i\hat{B}\psi_i \tag{2.87}$$

This shows that $\hat{B}\psi_i$ is an eigenfunction of the operator $\hat{A}$ with the eigenvalue a_i. This is possible only if $(\hat{B}\psi_i)$ is a multiple of ψ_i, i.e.

$$\hat{B}\psi_i = b_i\psi_i \tag{2.88}$$

In other words, ψ_i is also an eigenfunction of $\hat{B}$.

2.7.4 Conversely, if there exists a set of orthogonal functions ψ_i which are eigenfunctions of two operators $\hat{A}$ and $\hat{B}$, then they commute.

Proof: Let us expand any function Φ, in terms of the set of functions ψ_i and then operate on Φ with the commutator $[A, B]$.

$$[A, B]\Phi = (A\widehat{B - B}A)\Phi = (A\widehat{B - B}A)\sum_i C_i\psi_i$$

$$= \widehat{AB}\sum_i C_i\psi_i - \widehat{BA}\sum_i C_i\psi_i$$

$$= \sum_i C_i\hat{A}(\hat{B}\psi_i) - \sum_i C_i\hat{B}(\hat{A}\psi_i) \qquad (2.89)$$

Since $\hat{A}\psi_i = a_i\psi_i$ and $\hat{B}\psi_i = b_i\psi_i$, we can write Eq. (2.89) as

$$(A\widehat{B - B}A)\Phi = \sum_i C_iA(b_i\psi_i) - \sum_i C_i\hat{B}(a_i\psi_i)$$

$$= \Sigma C_ib_i(\hat{A}\psi_i) - \Sigma C_ia_i(\hat{B}\psi_i)$$

$$= \sum_i C_i(b_ia_i - a_ib_i)\psi_i$$

$$= 0 \qquad (2.90)$$

Since Φ is an arbitrary function, $A\widehat{B - B}A = 0$.

The physical implication of these last two theorems is important to note. If two operators are hermitian as they should always be if they are to represent two different physical properties and commute, then it is possible to have a system in which both the physical properties are simultaneously observable.

Let us consider the momentum of an electron in x-direction and its total energy. They are represented by the operators as

$$\hat{P}_x = \frac{h}{2\pi i}\frac{\partial}{\partial x}, \quad \hat{H} = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V$$

It can be shown for a function $\psi(x)$ describing an electron, that

$$\hat{P}_x\hat{H}\psi(x) = -\frac{h}{2\pi i}\cdot\frac{h^2}{8\pi^2 m}\frac{\partial^3\psi(x)}{\partial x^3} + \frac{h}{2\pi i}\frac{\partial V}{\partial x}\psi(x) + \frac{h}{2\pi i}\frac{\partial\psi(x)}{\partial x}\cdot V$$

and

$$\hat{H}\hat{P}_x\psi_{(x)} = -\frac{h^2}{8\pi^2 m}\frac{h}{2\pi i}\frac{\partial^3\psi(x)}{\partial x^3} + \frac{h}{2\pi i}V\frac{\partial\psi}{\partial x}$$

If $\frac{\partial V}{\partial x} = 0$, then

$$\hat{H}\hat{P}_x = \hat{P}_x\hat{H} \qquad (2.91)$$

If the potential energy does not change in the direction of the momentum of an electron, then it is possible to have the definite values of both the momentum and energy. On the other hand, the operators $\hat{P}_x$ and $\hat{X}$ are related as

$$\hat{P}_x\hat{X} - \hat{X}\hat{P}_x = \frac{h}{2\pi i} \qquad (2.92)$$

This shows that it is not possible to locate the position of a particle and to determine its momentum simultaneously without a certain degree of uncertainty. This is Heisenberg's uncertainty principle.

2.7.5 If $\hat{B}$ is an operator which commutes with an operator $\hat{A}$ (both being hermitian), ψ_1 and ψ_2 are the eigenfunctions of $\hat{A}$ and a_1 and a_2 are the corresponding eigenvalues respectively, then the integral $\int \psi_1^* \cdot \hat{B}\psi_2 \, d\tau$ vanishes.

Proof: We have $\hat{A}\psi_1 = a_1\psi_1$ and $\hat{A}\psi_2 = a_2\psi_2$. Consider the integral

$$\int \psi_1^* \hat{B}\hat{A}\psi_2 \, d\tau = \int \psi_1^* \hat{B}(a_2\psi_2) \, d\tau = a_2 \int \psi_1^* \hat{B}\psi_2 \, d\tau \tag{2.93}$$

Since $\hat{B}$ and $\hat{A}$ commute, we can write

$$\begin{aligned}\int \psi_1^* \cdot \hat{B}\hat{A}\psi_2 \, d\tau &= \int \psi_1^* \cdot \hat{A}\hat{B}\psi_2 \, d\tau = \int \psi_1^* \cdot \hat{A}(\hat{B}\psi_2) \, \partial\tau \\ &= \int (\hat{B}\psi_2) \cdot \hat{A}^* \psi_1^* \partial\tau = a_1 \int (\hat{B}\psi_2) \cdot \psi_1^* \partial\tau \\ &= a_1 \cdot \int \psi_1^* \hat{B}\psi_2 \partial\tau\end{aligned} \tag{2.94}$$

Therefore

$$a_2 \int \psi_1^* \cdot \hat{B}\psi_2 \partial\tau = a_1 \int \psi_1^* \cdot \hat{B}\psi_2 \partial\tau$$

or

$$(a_2 - a_1) \int \psi_1^* \hat{B}\psi_2 \partial\tau = 0 \tag{2.95}$$

If

$$a_1 \neq a_2, \quad \int \psi_1^* \hat{B}\psi_2 \partial\tau = 0 \tag{2.96}$$

However, this argument may not be valid if $a_1 = a_2$.

2.8 Eigenfunctions of the Position Operator and Dirac Delta Function

In quantum mechanics most of the properties represented by hermitian operators have discrete eigenvalues. In such cases we say that the property has a discrete eigenspectrum. Any arbitrary function can be expanded in terms of the orthonormal functions as given by Eq. (2.86). Since the function Φ must be normalised we have

$$\sum_i | C_i^2 | = 1 \tag{2.97}$$

If we multiply both sides of Eq. (2.86) by an eigenfunction ψ_j and then integrate over all space

$$\int \Phi\psi_j \, d\tau = \sum_i C_i \int \psi_i\psi_j \, d\tau = \sum_i C_i\delta_{ij} = C_j \tag{2.98}$$

where δ_{ij} is Kronecker's delta defined already in Sec. 2.7.2.

There are, however, some properties like the positional coordinates of a particle whose eigenvalues may have a continuous range. In such cases an arbitrary wave function $\psi(x)$ can be written as

$$\psi(x) = \int C_a \cdot \psi_a(x)\, da \tag{2.99}$$

where we consider the position of a particle on the x-axis and $\psi_a(x)$ is the eigenfunction of the position operator $\hat{x}$ with the eigenvalue a. In Eq. (2.99) the integration is extended over the whole range of eigenvalues of the position operator $\hat{x}$. Here the eigenfunctions of a continuous eigenspectrum cannot be normalised to unity. Instead, we normalise the function $\psi_a(x)$ in such a way that $| C_a |^2\, da$ gives the probability that the physical quantity in the state given by $\psi(x)$ has a value between a and $a + da$. Since the sum of the probabilities of all possible values of a must equal unity, we have

$$\int | C_a |^2\, da = 1 \tag{2.100}$$

One can normalise the arbitrary function $\psi(x)$ of Eq. (2.99) as

$$\int \psi^*(x)\psi(x)\, dx = \int | C_a |^2 da \tag{2.101}$$

From Eq. (2.99) one can also write

$$\int \psi^*(x)\psi(x)\, dx = \iint C_a^* \psi_a^*(x) \cdot \psi(x) da\, dx \tag{2.102}$$

By comparing these two equations we find

$$C_a = \int \psi_a^*(x)\psi(x)\, dx \tag{2.103}$$

in exact analogy to Eq. (2.98).

We shall now deal with Dirac delta function. Let us first define the Heaviside step function $H(x - a)$ as shown in Fig. 2.1.

where

$$\begin{aligned} H(x-a) &= 1 & x &> a \\ H(x-a) &= 0 & x &< a \\ H(x-a) &= 0.5 & x &= a \end{aligned} \tag{2.104}$$

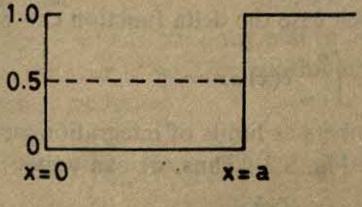

Fig. 2.1 *Heaviside step function.*

We, then, define Dirac delta function $\delta(x - a)$ as the first derivative of the step function of Eq. (2.104).
Thus

$$\delta(x - a) = \frac{d}{dx}H(x - a) \tag{2.105}$$

One may now write

$$\begin{aligned} \delta(x - a) &= 0 \qquad x > a \\ \delta(x - a) &= 0 \qquad x < a \\ \delta(x - a) &= \infty \qquad x = a \end{aligned} \tag{2.106}$$

Consider the following integral

$$\int_{-\infty}^{\infty} f(x)\delta(x - a)\, dx$$

which we evaluate by parts. We have

$$\begin{aligned} \int_{-\infty}^{\infty} f(x)\delta(x - a)\, dx &= \Big[f(x)H(x - a)\Big]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} H(x - a)\frac{df(x)}{dx}\, dx \\ &= f(\infty).1 - f(-\infty).0 - \int_{-\infty}^{a} H(x - a)\, \frac{df(x)}{dx}\, dx \\ &\quad - \int_{a}^{\infty} H(x - a)\, \frac{df(x)}{dx}\, dx \end{aligned}$$

Since

$$\begin{aligned} H(x - a) &= 0 \qquad \text{for } x < a \\ H(x - a) &= 1 \qquad \text{for } x > a \end{aligned}$$

$$\begin{aligned} &= f(\infty) - \Big[f(x)\Big]_{a}^{\infty} \\ &= f(\infty) - f(\infty) + f(a) \\ &= f(a) \end{aligned} \tag{2.107}$$

If we compare Eq. (2.107) with Eq. (2.98) we see that the delta function plays the same role in an integral as Kronecker's delta does in a summation. When $f(x) = 1$, we can show that

$$\int_{-\infty}^{\infty} \delta(x - a)\, dx = 1 \tag{2.108}$$

This means that the delta function is zero everywhere except at the singular point $x = a$ where its amplitude becomes infinite [Eq. (2.106)] so that the function has unit area. It is often convenient to place the origin at the singular point in which case the delta function can be written as

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1$$

We can take any numbers as limits of integration but the point $x = 0$ must lie between them (see Fig. 2.2). Thus, we can write

$$\int_{-b}^{+b} \delta(x)\, dx = 1 \tag{2.109}$$

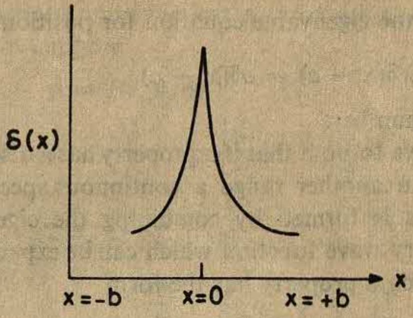

Fig. 2.2 *The area under the curve is unity.*

Now we consider the operator equation for position as

$$\hat{X}\psi_a(x) = a\psi_a(x) \tag{2.110}$$

where a is the eigenvalue. One may write Eq. (2.110) as

$$(\hat{X} - a)\psi_a(x) = 0 \tag{2.111}$$

Since the operation corresponding to position is simply the multiplication by the variable itself we have

$$\hat{X} = x \tag{2.112}$$

and conclude that if $x \neq a, \psi_a(x) = 0$. Since that an eigenfunction is zero everywhere is unacceptable we have $\psi_a(x) \neq 0$ for $x = a$. This means that if $\psi_a(x)$ is an eigenfunction of $\hat{x}$ with eigenvalue a, measurement of the position on the x-axis gives the value a in the state described by $\psi_a(x)$. This is true if the probability density, $|\psi_a(x)|^2$ is zero everywhere except at $x = a$. It is, thus, clear that one can now write the eigenfunction $\psi_a(x)$ as

$$\psi_a(x) = \delta(x - a) \tag{2.113}$$

To verify this we deal with $|C_a|^2\, da$ which may be written from Eq. (2.103) as

$$\begin{aligned} |Ca|^2\, da &= \left| \int_{-\infty}^{\infty} \psi_a^*(x)\cdot\psi(x)\, dx \right|^2 da \\ &= \left| \int_{-\infty}^{\infty} \delta(x - a)\psi(x)\, dx \right|^2 da \qquad \text{[Using Eq. (2.113)]} \\ &= |\psi(a)|^2\, da \qquad \text{[Using Eq. (2.107)]} \end{aligned} \tag{2.114}$$

Since the quantity a in $\delta(x - a)$ can have any real value, the eigenvalues of x form a continuum in $-\infty < a < \infty$. The continuum eigenfunctions are not quadratically integrable, we have

$$\begin{aligned} \int_{-\infty}^{\infty} |\delta(x - a)|^2\, dx &= \int_{-\infty}^{\infty} \delta(x - a)\delta(x - a)\, dx \\ &= \delta(a - a) = \delta(0) = \infty \qquad \text{[From Eq. (2.106)]} \end{aligned}$$

One can summarise the eigenvalue equation for position as

$$\hat{X}\delta(x - a) = a\delta(x - a) \tag{2.115}$$

where a is any real number.

It is also instructive to note that if a property has a discrete eigenspectrum in one range and in another range a continuous spectrum the complete system of functions is formed by combining the eigenfunctions of both spectra. Any arbitrary wave function which can be expanded in terms of the eigenfunctions of such a property has the form

$$\psi(x) = \sum_i C_i\psi_i(x) + \int C_a\psi_a(x)\,da \tag{2.116}$$

where the summation extends over the discrete spectrum and the integral over the continuum.

APPENDIX 2

Equations for the transformations from three dimensional rectangular coordinates to spherical polar coordinates are as follows (Fig. A2.1)

$$\left.\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}\right\} \tag{A2.1}$$

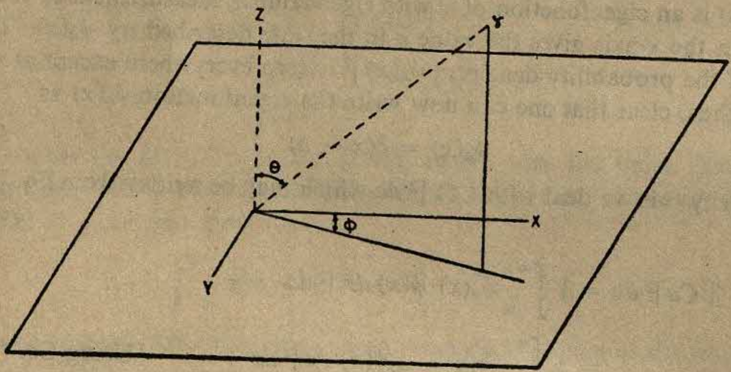

Fig. A2.1

where the new coordinates r, θ and ϕ are shown in Fig. A2.1. From the set of equations (A2.1), we obtain

$$\left.\begin{aligned} r^2 &= x^2 + y^2 + z^2 \\ \cos\theta &= \frac{z}{(x^2 + y^2 + z^2)^{1/2}} \\ \tan\phi &= y/x \end{aligned}\right\} \tag{A2.2}$$

Any quantity expressed in spherical polar coordinates will be a function of r, θ and ϕ. Let us suppose

$$\psi = f(r, \theta, \phi)$$

then
$$\partial\psi = \frac{\partial\psi}{\partial r}dr + \frac{\partial\psi}{\partial\theta}d\theta + \frac{\partial\psi}{\partial\phi}d\phi \qquad (A2.3)$$

or
$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial x} \qquad (A2.4)$$

and
$$\frac{\partial}{\partial y} = \frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial}{\partial\phi}\frac{\partial\phi}{\partial y} \qquad (A2.5)$$

Using the set of equations in (A2.2) and in (A2.1) we obtain

$$\left.\begin{aligned}
&\frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\cos\phi \\
&\frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta\sin\phi \\
&\frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r}, \ \frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r} \\
&\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta} \\
&\frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\sin\theta}
\end{aligned}\right\} \qquad (A2.6)$$

Therefore,

$$\begin{aligned}
\hat{L}_z &= \frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \\
&= \frac{h}{2\pi i}\left[r\sin\theta\cos\phi\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right. \\
&\quad \left. - r\sin\theta\sin\phi\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right] \\
&= \frac{h}{2\pi i}\frac{\partial}{\partial\phi} \qquad (A2.7)
\end{aligned}$$

Following the similar procedure, the expressions for $\hat{L}_x$ and $\hat{L}_y$ and hence $\hat{L}^2$ can be obtained.

PROBLEMS

1. **Show that the eigenfunctions belonging to different eigenvalues of a unitary operator are mutually orthogonal.**
2. **Find the eigenfunctions of a linear momentum operator, say $\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)$ Show that in the absence of any restriction eigenvalues of linear momentum form a continuous spectrum.**

3. Show that if ψ is an eigenfunction of $\hat{A}$ with the eigenvalue a, then it is also an eigenfunction of $\exp(A)$ with eigenvalue $\exp(a)$.
4. Show that $[x^n, Px] = \frac{h}{2\pi i} n x^{n-1}$ where n is a positive integer.
5. Show that (a) the product of two hermitian operators is hermitian if they commute, and (b) the inverse of a hermitian operator is hermitian.
6. Find the normalised eigenfunction of the operator $\hat{L}_z$ [see Eqs. (2.53) and (2.54)].
7. Show that the operator $\hat{L}_z$ commutes with with $\hat{L}^2$.
8. Show that the following mathematical function has the properties of Dirac delta function

$$\delta(x) = \underset{n \to \infty}{\mathrm{Lt}} \left(\frac{n}{\pi}\right)^{1/2} \cdot \exp(-nx^2)$$

9. We define a translation operator $\hat{T}$ by

$$\hat{T}_a f(x) = f(x + a)$$

(a) Is $\hat{T}_a$ a linear operator?

(b) Evaluate $(\hat{T}_1^2 - 3\hat{T}_1 + 2)x^2$

10 An operator $\hat{P}$ has discrete eigenvalues and a property

$$\hat{P}^2 = \hat{P}$$

Find its possible eigenvalues.

3

Wave Mechanics of Some Simple Systems with Constant Potential Energy

3.1 Introduction

It is possible to deal with, by the methods of quantum mechanics, certain simple systems for which the Schrödinger equation can be solved exactly and in which the potential energy can be chosen either constant or zero. These systems may be so different from the naturally occurring systems of physical and chemical interest that one might think that they can hardly be of any value. However, this is not the case since the exact solutions of most physical and chemical systems have not been obtained. On the other hand, the exact quantum mechanical solution of the simple and ideal systems provides us with sufficient insight that helps in the interpretation of the behaviour of more complex systems occurring in nature.

As an example, we consider the exact solution of Schrödinger's equation for a system of an electron confined in a box in which the potential energy is either zero or constant and infinite everywhere else outside the box. The mathematics is simple for this system but the results illustrate some important properties of quantum mechanical systems, such as quantisation of energy, quantum numbers, zero point energy, etc. In fact, this system provides the basis of the free electron approximation to molecular orbitals which we shall deal with in a later chapter.

3.2 One Dimensional Box

Suppose an electron of mass m_e is constrained to move in the x-direction from $x = 0$ to $x = a$. Outside this region the potential energy, V is taken to be infinite, and within this region it is zero (Fig. 3.1).

Outside the box (Fig. 3.1) the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2}(E - \infty)\psi = 0 \qquad (3.1)$$

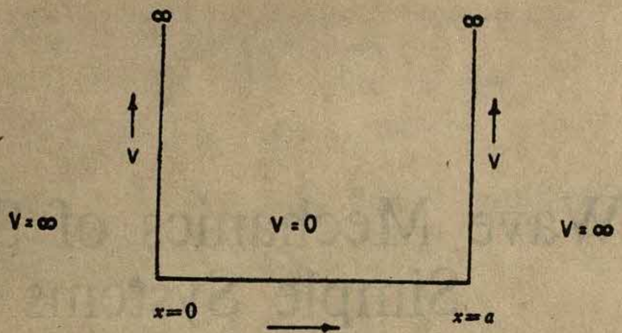

Fig. 3.1 *One dimensional box*

This equation is satisfied if ψ is zero at all points outside the box. In other words electron cannot be found at all outside the box.

Inside the box (Fig. 3.1) the wave equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2} E\psi = 0 \tag{3.2}$$

Equation (3.2) may be written in the operator form

$$\hat{H}\psi = E\psi \quad \text{where} \quad H = -\frac{h^2}{8\pi^2 m_e}\frac{d^2}{dx^2}$$

According to one of the postulates of quantum mechanics (2.4), the mean value of E is observable and independent of the coordinate of the electron. Henceforth, we refer to E as the mean value of energy and assume,

$$\frac{8\pi^2 m_e}{h^2} E = k^2 \tag{3.3}$$

where k^2 is a constant independent of x. Eq. (3.2) can be written as

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{3.4}$$

which is identical in form to the equation solved in Appendix 1 and has the solution that may be written as

$$\psi = C \cos kx + D \sin kx \tag{3.5}$$

According to the laws of quantum mechanics, ψ must be a continuous function of x. Therefore, it must be consistent with the solution found for the outside of the box, hence at the walls of the box, i.e. at $x = 0$ and at $x = a$, ψ must be zero.

From the boundary conditions, $\psi = 0$ at $x = 0$ we see that $C = 0$ and from the condition, $\psi = 0$ at $x = a$, we have

$$D \sin ka = 0 \tag{3.6}$$

or

$$\sin ka = 0 \quad \text{or} \quad ka = n\pi \tag{3.7}$$

$$n = 0, 1, 2, 3, 4, \ldots$$

where n is called quantum number which is either zero or a positive integer. Thus, the permitted solutions are

$$\psi_n = D \sin \frac{n\pi}{a} x \tag{3.8}$$

and the energy E follows from Eqs. (3.3) and (3.7) and is given by

$$E = \frac{k^2h^2}{8\pi^2 m_e} = \frac{n^2h^2}{8m_e a^2} \tag{3.9}$$

If the potential energy inside the box is not zero but constant equal to say, V, then the energy spectrum is given by

$$E = \frac{n^2h^2}{8m_e a^2} + V \tag{3.10}$$

Although the value zero for n is permitted it is not acceptable because the function ψ_n of Eq. (3.8) then becomes zero; but an electron is assumed to be always present inside the box. Therefore, the lowest kinetic energy, called the zero-point energy, of an electron in a box is given by [substitute $n = 1$ in Eq. (3.9)]

$$E_{\text{zero point}} = \frac{h^2}{8m_e a^2} \tag{3.11}$$

This shows that the electron inside the box is not at rest even at 0°K. Therefore, the position of the electron cannot be precisely known. Since only the mean value of the kinetic energy is known, the momentum of the electron is also not precisely known (see answer to problem 2 of this chapter). The occurrence of the zero-point energy is therefore in accordance with the Heisenberg uncertainty principle.

If the walls of the box are removed and an electron is free to move without any restriction in a field whose potential energy may be assumed to be zero then Schrödinger's equation and its solutions are respectively given by the Eqs. (3.2) and (3.5). The arbitrary constants C, D and k^2 can now have any value one chooses to give them. Therefore, the energy given by

$$E = \frac{k^2h^2}{8\pi^2 m_e} \tag{3.12}$$

is not quantised in this case. Thus, when an electron is bound in a system it has quantised energy levels given by Eq. (3.9) or (3.10) and it leads to discrete spectrum. On the other hand, a free electron moving without any restriction has the continuous energy spectrum. This qualitatively explains the occurrence of continuum in the atomic or molecular spectra on ionisation because an electron lost by an atom or molecule is free to move without any restriction.

3.3 Normalisation and Orthogonality

The wave functions for the various states of an electron in a box are given by Eq. (3.8). The probability distribution is

$$|\psi_n^2| = D^2 \sin^2 \frac{n\pi}{a}x \tag{3.13}$$

The integral of this wave function over the entire space in the box must be equal to unity because there is only one electron and at all times it is somewhere in the box. Therefore

$$\int_0^a |\psi_n^2|\, dx = \int_0^a D^2 \sin^2 \frac{n\pi}{a}x\, dx = 1$$

But, $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$

So
$$\int_0^a |\psi_n^2|\, dx = D^2\left[\frac{1}{2}\int_0^a dx - \frac{1}{2}\int_0^a \cos\frac{2n\pi}{a}x\, dx\right]$$
$$= D^2[a/2 - 0] = 1$$

or
$$D = \sqrt{\frac{2}{a}} \tag{3.14}$$

Thus, the normalised wave function of an electron in a one-dimensional box is given by

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \tag{3.15}$$

Consider the normalised wave functions ψ_n and $\psi_{n'}$ corresponding to two different states of an electron in a box. It is found that for $n \neq n'$

$$\int_0^a \psi_n\psi_{n'} dx = 0 \tag{3.16}$$

The wave functions for different states of this system are thus orthogonal. This can be shown as follows[1]

$$\int_0^a \psi_n\psi_{n'}\, dx = \frac{2}{a}\int_0^a \sin\frac{n\pi}{a}x \times \sin\frac{n'\pi}{a}\, dx$$
$$= \frac{1}{a}\int_0^a \left\{\cos\,(n - n')\pi\frac{x}{a} - \cos\,(n + n')\pi\frac{x}{a}\right\}dx$$
$$= \frac{1}{a\pi}\left[\frac{a}{(n-n')}\cdot\sin\frac{(n-n')\pi x}{a} - \frac{a}{(n+n')}\cdot\sin\frac{(n+n')\pi x}{a}\right]_0^a$$
$$= 0 \tag{3.17}$$

Since the hamiltonian for an electron in a box is a hermitian operator, the wave function ψ_n and ψ_n' corresponding to two different states should be orthogonal in accordance with the theorem of Sec. 2.7.1. This property of orthogonality between any two different states ensures that the various states are truly independent of one another.

---

[1] $\sin n\theta \sin n'\theta = \frac{1}{2}[\cos\,(n - n')\theta - \cos\,(n + n')\theta]$.

3.4 Characteristics of the Wave Functions

A few energy levels and the corresponding wave functions are shown graphically in Fig. 3.2. Imagine a one dimensional mirror which is parallel to the walls of the box and situated at the centre of the box as shown by the dotted line in Fig. 3.2. It should be noted that the wave functions are alternately symmetrical and antisymmetrical with respect to reflection from such a mirror.

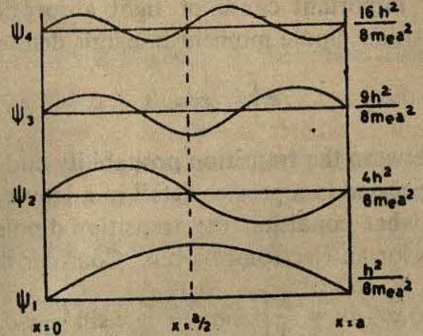

Fig. 3.2 *Energy levels and eigenfunctions for a few lowest levels of an electron in a one-dimensional box of length a*

Besides the points on the walls of the box, there are points inside the box where the wave function is zero. These points are called nodes. It is evident from Fig. 3.2 that as the quantum number, n increases, the number of nodes on the wave increases. For example, the state whose wave function is ψ_n has $(n-1)$ nodes inside the box. This type of behaviour is general for all systems. Increasing the number of nodes decreases the wavelength, which corresponds to increasing the kinetic energy.

3.5 Discussion of the Factors Influencing Colour

The wave mechanical treatment of an electron in a box gives rise to large number of discrete energy levels. On suitable excitation the electron may undergo transition from one level to another. The transition energy for the transition

$\psi_{n'} \rightarrow \psi_n$ is given by

$$\Delta E = \frac{n'^2 - n^2}{8m_ea^2} \cdot h^2 \tag{3.18}$$

The frequency of transition obtained through Bohr's relation, $\nu = \Delta E/h$, is given by

$$\nu = \frac{n'^2 - n^2}{8m_ea^2} \cdot h \tag{3.19}$$

or the wavelength of the transition is

$$\lambda = \frac{c}{\nu} = \frac{8m_eca^2}{(n'^2 - n^2)h} \tag{3.20}$$

This relation shows that the longer the length of the box a, the longer the wavelength at which the optical transition in such a system occurs. Thus, by suitably adjusting the length of the box, the wavelength of an electronic transition can be made to appear in the visible range of the spectrum (roughly from 4000–8000 Å). The system then becomes coloured. However, it should be emphasized now that transition between any two levels is not always permissible, because the transition probability for an electric dipole transition (which is the most important cause of light absorption) depends on the magnitude of transition dipole moment integrals defined as

$$e\int \psi_{n'}\hat{x}\psi_n\,dx$$

The relationship between the transition probability and the transition dipole moment will be discussed in a greater detail in a later chapter. Here, it will be shown, under what condition the transition dipole moment integral is different from zero for an electron-in-a-box. Consider the integral

$$\int_0^a \psi_{n'}\cdot\hat{x}\psi_n\,dx = \frac{2}{a}\int_0^a \sin\frac{n'\pi}{a}x\cdot\hat{x}\sin\frac{n\pi}{a}x\,dx \tag{3.21}$$

Letting $\frac{\pi x}{a} = \theta$, we may write

$$\int_0^a \psi_{n'}\hat{x}\psi_n\,dx = \frac{2a}{\pi^2}\int_0^\pi \sin n\theta\sin n'\theta\cdot\theta\,d\theta$$

$$= \frac{2a}{\pi^2}\left[\frac{1}{2}\int_0^\pi \cos(n-n')\theta\cdot\theta\,d\theta - \frac{1}{2}\int_0^\pi \cos(n+n')\,\theta\cdot\theta\,d\theta\right]$$

$$= \frac{a}{\pi^2}[I_1 - I_2] \tag{3.22}$$

where

$$I_1 = \int_0^\pi \cos(n-n')\,\theta\cdot\theta\,d\theta$$

$$= \left[\theta\cdot\frac{\sin(n-n')\theta}{(n-n')}\right]_0^\pi - \int_0^\pi \frac{\sin(n-n')\theta}{n-n'}\,d\theta$$

$$= \left[0 + \frac{1}{(n-n')^2}(-2)\right],\quad \text{if } (n-n') \text{ is an odd number}$$

$$= 0,\quad \text{if } (n-n') \text{ is an even number;}$$

and

$$I_2 = \int_0^\pi \cos(n+n')\,\theta\cdot\theta\,d\theta$$

$$= \left[\theta\cdot\frac{\sin(n+n')\theta}{n+n'}\right]_0^\pi - \int_0^\pi \frac{\sin(n+n')\theta}{(n+n')}\,d\theta$$

$$= \left[0 - \frac{2}{(n+n')^2}\right],\qquad \text{if } (n+n') \text{ is an odd number} \tag{3.24}$$

$$= 0,\qquad \text{if } (n+n') \text{ is an even number.}$$

This simple argument shows that the transition dipole integral $\int \psi_{n'} \hat{x} \psi_n \, dx$ does not vanish if $(n \pm n')$ is an odd number. Then the selection rule for an electric dipole transition in this system may be stated as follows: *A transition between a pair of states is possible if the sum of or difference in quantum numbers is an odd number. If both are even numbers the transition is said to be strictly forbidden.*

3.6 Symmetry Arguments in Deriving the Selection Rule

Instead of evaluating the transition dipole integral, simple symmetry arguments may be used to predict whether an electric dipole transition is allowed or forbidden. A symmetry operation is a process, such as rotation about an axis, reflection from a plane mirror, etc., that transforms a system into a form indistinguishable from its original. Any integral, say $\int_0^\infty f(x)\, dx$, which stands for an observable quantity such as energy, must be independent of the coordinate system and invariant to any symmetry operation. For example, in Fig. 3.3 is shown the transformation of rotation about z-axis on the coordinate system. The area under the curve determines the magnitude of the integral $\int_0^\infty f(x)\, dx$, which remains unchanged on rotation. If the integrand changes sign under a symmetry operation, it will have a value in one part of space, equal and opposite to that in another part of space. The integral overall space would then be zero. Hence a non-vanishing transition moment integral, $\int \psi_{n'} \bar{x} \psi_n dx$ must remain unchanged on a symmetry operation.

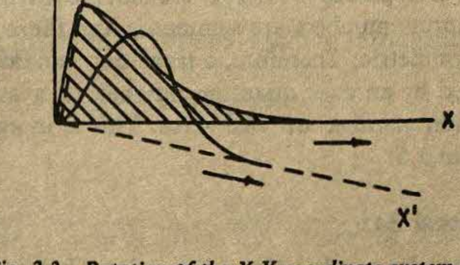

Fig. 3.3 *Rotation of the X-Y coordinate system by an arbitrary angle about Z-axis which is perpendicular to the plane of the paper*

Let $\hat{R}$ represent the reflection from a plane mirror situated at the centre of, and parallel to the walls of, the box in the system of an electron in a box (Fig. 3.2). An eigenvalue equation for such an operator may be written as

$$\hat{R}\psi = \alpha\psi \tag{3.25}$$

where α is the eigenvalue of $\hat{R}$. Since the repetition of this operation yields the original ψ one may write

$$\hat{R}^2\psi = \hat{R}\hat{R}\psi = \hat{R}\alpha\psi = \alpha\hat{R}\psi = \alpha^2\psi = \psi \tag{3.26}$$

or

$$\alpha^2 = 1, \qquad \alpha = \pm 1 \tag{3.27}$$

Thus, there are only two possible eigenvalues of $\hat{R}$. When $\alpha = +1$, the eigenfunction is said to be symmetric with respect to the operation $\hat{R}$ and for $\alpha = -1$, the eigenfunction is antisymmetric. Let the symmetric and antisymmetric wave functions of the electron-in-a-box system be, respectively, denoted by ψ_S and ψ_A.

Consider the integral $\int \psi_s \bar{x} \psi_s \, dx$. On operation with $\hat{R}$, one has

$$\begin{aligned} \hat{R}\int \psi_s \bar{x} \psi_s \, dx &= \int \hat{R}\psi_s \cdot \hat{R}\bar{x} \cdot \hat{R}\psi_s \, dx \\ &= \int \psi_s(-\bar{x})\, \psi_s \, dx \\ &= -\int \psi_s \bar{x} \psi_s \, dx \end{aligned} \tag{3.28}$$

Thus the integral changes sign and therefore a transition from a symmetric state to another symmetric state is forbidden. Similarly, it can be shown that a transition from an antisymmetric state to another antisymmetric state is also forbidden, while the transition from a symmetric state to an antisymmetric state is allowed because the integral $\int \psi_s \bar{x} \psi_A \, dx$ is unchanged under the operation $\hat{R}$. It is apparent from Fig. 3.2 that the wave functions characterised by odd quantum numbers are symmetric and those by even quantum numbers are antisymmetric. Therefore, a transition can take place only from a state characterised by an even quantum number to a state characterised by an odd quantum number or vice versa. This is in agreement with the conclusion drawn in 3.5.

3.7 Three Dimensional Box

We now consider an electron in a three-dimensional box which for simplicity is taken to be a cubic box with edges of length a and volume of a^3 (Fig. 3.4).

The potential V may be put equal to zero within the box; at the boundaries of the box and in the remainder of space outside the box, we assume, $V = \infty$. We choose the Cartesian coordinate system with the origin at one corner of the box and the x, y and z axes along the edges of length a each, as shown in Fig. 3.4. The potential energy is then

$$V_x = 0, \quad 0 < x < a, \quad V_x = \infty \quad \text{otherwise}$$
$$V_y = 0, \quad 0 < y < a, \quad V_y = \infty \quad \text{otherwise}$$
$$V_z = 0, \quad 0 < z < a, \quad V_z = \infty \quad \text{otherwise}$$

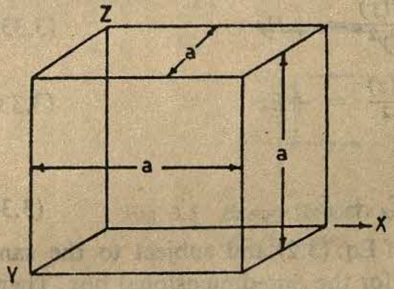

Fig. 3.4 *Electron in a three-dimensional cubic box*

The Schrödinger equation within the box is then given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m_e}{h^2} E\psi = 0 \tag{3.29}$$

We assume the possibility that the wave function ψ which is a function of x, y, z [i.e. $\psi(x, y, z)$] is a product of three parts separately dependent on x, y, and z, as

$$\psi(x, y, z) = f(x)f(y)f(z) \tag{3.30}$$

Therefore

$$\left.\begin{aligned} \frac{\partial^2\psi}{\partial x^2} &= f(y)f(z)\frac{\partial^2 f(x)}{\partial x^2} \\ \frac{\partial^2\psi}{\partial y^2} &= f(x)f(z)\frac{\partial^2 f(y)}{\partial y^2} \\ \frac{\partial^2\psi}{\partial z^2} &= f(x)f(y)\frac{\partial^2 f(z)}{\partial z^2} \end{aligned}\right\} \tag{3.31}$$

Substituting Eqs. (3.31) in (3.29) and dividing throughout by

$$\frac{8\pi^2 m_e}{h^2} f(x)f(y)f(z)$$

one gets

$$\frac{h^2}{8\pi^2 m_e}\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2} + \frac{h^2}{8\pi^2 m_e}\frac{1}{f(y)}\frac{\partial^2 f(y)}{\partial y^2} + \frac{h^2}{8\pi^2 m_e}\frac{1}{f(z)}\frac{\partial^2 f(z)}{\partial z^2} + E = 0 \tag{3.32}$$

The first term is a function of x only, and independent of y and z, the second term is a function of y only and independent of x and z, and the third is a function of z, independent of x and y. The fourth is a constant. If y and z are kept constant and x varied, the second, third and fourth terms remain constant. Therefore first term must remain constant. Let this constant be—E_x. By a similar argument the second must be constant, say—E_y, and the third, say—E_z. We may, therefore, write

$$-\frac{h^2}{8\pi^2 m_e}\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2} = +Ex \tag{3.33a}$$

$$-\frac{h^2}{8\pi^2 m_e}\frac{1}{f(y)}\frac{\partial^2 f(y)}{\partial y^2} = +Ey \tag{3.33b}$$

$$-\frac{h^2}{8\pi^2 m_e}\frac{1}{f(z)}\frac{\partial^2 f(z)}{\partial z^2} = +Ez \tag{3.33c}$$

and also

$$E = E_x + E_y + E_z \tag{3.34}$$

Each of the Eqs. (3.33) is of the form of Eq. (3.2) and subject to the same boundary conditions as assumed earlier for the one-dimensional box. Therefore, the normalised wave functions and the energy spectrum associated with Eq. (3.33a) are given by

$$f(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi}{a}x \tag{3.35}$$

and

$$E_x = \frac{n_x^2 h^2}{8m_e a^2} \tag{3.36}$$

where n_x is an integer not including zero as this value of n_x would make $f(x)$ equal to zero everywhere. There are similar solutions for $f(y)$ and $f(z)$ which involve the quantum numbers n_y and n_z. The final result is therefore,

$$\begin{aligned}\psi(x, y, z) &= f(x)f(y)f(z)\\ &= \sqrt{\frac{8}{a^3}}\sin\frac{n_x\pi}{a}x\sin\frac{n_y\pi}{a}y\sin\frac{n_z\pi}{a}z\end{aligned} \tag{3.37}$$

and

$$E = E_x + E_y + E_z = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8m_e a^2} \tag{3.38}$$

where $n_x, n_y, n_z = 1, 2, 3, 4, \ldots$ The occurrence of three quantum numbers is characteristic of a three-dimensional problem in wave mechanics. The zero point energy is three times that for a one dimensional box, there being a part associated with each of the three coordinates. Since each state is characterised by three quantum numbers it is possible to construct several excited states of same energy. For example, there are three independent states having the quantum numbers (2, 1, 1), (1, 2, 1) and (1, 1, 2) for (n_x,

n_y, n_z). All these three states have the same energy $6h^2/8m_ea^2$. Such a level is said to be three-fold degenerate or triply degenerate. In Fig. 3.5 is shown a few energy levels illustrating the degeneracy and the zero point energy.

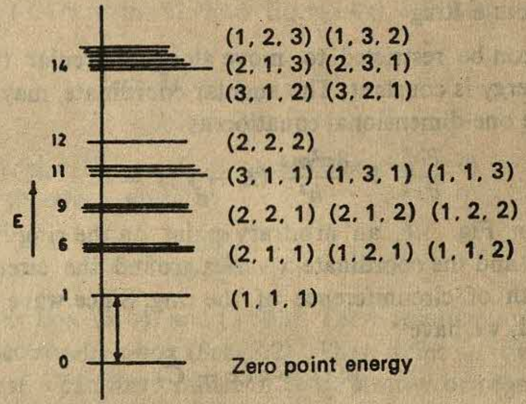

Fig. 3.5 *Energy (in units of $h^2/8m_ea^2$) and degeneracy of the various states*

The wave functions of the three members of the above triply degenerate levels are different. Consider a slight distortion of the cube by *da* along the *x*-axis. For the state (2, 1, 1) the energy of electron in the undistorted cube may be written as

$$\begin{aligned} E &= E_x + E_y + E_z \\ &= \frac{4h^2}{8m_ea^2} + \frac{h^2}{8m_ea^2} + \frac{h^2}{8m_ea^2} \end{aligned} \tag{3.39}$$

The new energy on distortion along the *x*-axis is

$$\begin{aligned} E + dE &= E_x + dE_x + E_y + E_x \\ &= \frac{4h^2}{8m_ea^2} - \frac{h^2}{m_ea^3}\,da + \frac{h^2}{8m_ea^2} + \frac{h^2}{8m_ea^2} \\ &= \frac{6h^2}{8m_ea^2} - \frac{h^2}{m_ea^3}\,da \end{aligned} \tag{3.40}$$

whereas the new energy for the other two states, i.e. ψ (1, 2, 1) and ψ (1, 1, 2) is

$$E + dE = \frac{6h^2}{8m_ea^2} - \frac{h^2}{4m_ea^3}\,da \tag{3.41}$$

Thus, the initial three-fold degenerate levels are split on distortion of the cube into a non-degenerate level and doubly degenerate levels. It is a common phenomenon in chemistry that the electronic degeneracy is reduced or removed on slight distortion of a system. This is analogous to the *Jahn-Teller effect* which states that *in a non-linear molecule where electronic degeneracy occurs there always exists a vibrational mode which can remove the degeneracy*. The molecule can, therefore, spontaneously distort from its most symmetric configuration until it assumes a configuration of lower symmetry and lower energy.

3.8 Electron in a Ring

Let an electron be restricted to move along a circular track on which the potential energy is constant. The angular coordinate may be used but we shall use the one-dimensional equation as

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2}(E - V)\psi = 0 \tag{3.42}$$

As shown in Fig. 3.6, an arbitrary point on the ring is chosen as origin (i.e., $x = 0$) and the coordinate x varies around the circular track. Let C be the length of circumference of the ring. Since wave functions must be single valued, we have

$$\psi(x) = \psi(x + C) \tag{3.43}$$

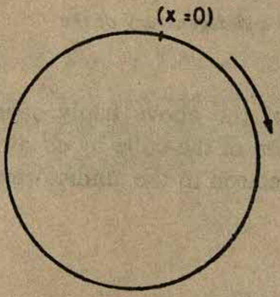

Fig. 3.6 *Electron moving in a ring of constant potential energy*

Setting the potential energy, V equal to zero and assuming

$$\frac{8\pi^2 m_e}{h^2} E = k^2 \tag{3.44}$$

the general solution of Eq. (3.42) becomes

$$\psi = A \sin kx + B \cos kx \tag{3.45}$$

The boundary conditions are now different from those of a one-dimensional box (Fig. 3.2). According to Eq. (3.43)

$$\psi(0) = \psi(C) \tag{3.46}$$

Therefore,

$$B = A \sin kC + B \cos kC \tag{3.47}$$

With the particle in a box there was a discontinuity in $\partial\psi/\partial x$ at the walls of the box because at those points there was a discontinuity in the potential energy. In such a situation while ψ is continuous, $\partial\psi/\partial x$ is not. Where there is no discontinuity in V, as is in this case, both ψ and $\partial\psi/\partial x$ must be continuous. Thus, we have another condition

$$\left(\frac{\partial\psi}{\partial x}\right)_{x=0} = \left(\frac{\partial\psi}{\partial x}\right)_{x=C} \tag{3.48}$$

This leads to

$$Ak = Ak \cos kC - Bk \sin kC \tag{3.49}$$

Multiplying Eq. (3.47) with Bk and Eq. (3.49) with A and then adding them, we obtain

$$\cos kC = 1 \tag{3.50a}$$

or

$$kC = 2n\pi \tag{3.50b}$$

where $n = 0 \pm 1, \pm 2, \pm 3, \pm 4, \ldots$, because $\cos(-\theta) = \cos\theta$. The energy levels are, therefore, given by

$$E = \frac{n^2h^2}{2m_eC^2} \tag{3.51}$$

which follows from Eqs. (3.44) and (3.50b). These results may be compared with that of an electron-in-a-box (Sec. 3.2). They differ in two important aspects. In this case n can have values of zero, positive or negative integers so that each energy level, except that for $n = 0$, is doubly degenerate. The unnormalised wave functions may be written as

$$\psi = A \sin \frac{2n\pi}{C} x + B \cos \frac{2n\pi}{C} x \tag{3.52}$$

which follows from Eqs. (3.45) and (3.50b). For a state having $n = 0$ (for which $E = 0$), the wave function is

$$\psi_0 = B = \text{constant} \tag{3.53}$$

There is, therefore, no variation of ψ round the ring in the lowest state. Thus, the zero point energy is not encountered with when the potential energy does not change round the circular track. This does not violate the uncertainty principle because the particle can be found anywhere in the ring with equal probability and therefore the uncertainty in position is infinite.

The normalisation requirements provide a relationship between A and B as follows:

$$\int_0^C \left(A \sin \frac{2n\pi}{C} x + B \cos \frac{2n\pi}{C} x\right)^2 dx$$

$$= A^2 \int_0^C \sin^2 \frac{2n\pi}{C} x dx + B^2 \int_0^C \cos^2 \frac{2n\pi}{C} x dx$$

$$+ 2AB \int_0^C \sin \frac{2n\pi}{C} x \cos \frac{2n\pi}{C} x dx = 1$$

or

$$(A^2 + B^2)\, C/2 = 1$$

or

$$A^2 + B^2 = 2/C \tag{3.54}$$

The simplest way of representing A and B to satisfy Eq. (3.54) is to put

$$A = \sqrt{\frac{2}{C}} \cos\alpha, \quad B = \sqrt{\frac{2}{C}} \cdot \sin\alpha \tag{3.55}$$

where α may have any value.

Therefore the wave function

$$\psi = \sqrt{\frac{2}{C}} \cos \alpha \sin \frac{2n\pi}{C} x + \sqrt{\frac{2}{C}} \sin \alpha \cos \frac{2n\pi}{C} x$$

$$= \sqrt{\frac{2}{C}} \sin \left(\frac{2n\pi}{C} x + \alpha\right) \tag{3.56}$$

satisfies the wave equation (3.42) and is normalised.

3.9 The Rigid Rotator

More important and somewhat more complex than the systems discussed in the previous sections is the one dealing with the rotation of a diatomic molecule in space, where the bond length is assumed to remain unchanged during rotation. The theory of such rigid rotator in space is useful in dealing with rotational spectra of diatomic molecules. We consider a diatomic molecule which consists of two atoms of mass m_1 and m_2 rigidly joined by a weightless link of length R. Assume that the centre of gravity of the system is fixed at the origin of our coordinate system. Let the distance of m_1 from the centre of gravity be r_1 and distance of m_2 be r_2, then

$$m_1 r_1 = m_2 r_2$$

and

$$r_1 + r_2 = R$$

where

$$r_1 = \frac{m_2 R}{m_1 + m_2}$$

and

$$r_2 = \frac{m_1 R}{m_1 + m_2}$$

The kinetic energy of rotation of the atoms joined together by a link is given by

$$\text{KE} = \tfrac{1}{2} m_1 v_1^2 + \tfrac{1}{2} m_2 v_2^2 \tag{3.57}$$

where v_1 and v_2 are the linear velocities of mass m_1 and m_2 respectively. Since r_1 and r_2 are assumed to remain unchanged during rotation about the centre of gravity, one can write

$$\text{KE} = \tfrac{1}{2} m_1 \omega^2 r_1^2 + \tfrac{1}{2} m_2 \omega^2 r_2^2 = \tfrac{1}{2} \omega^2 I = \frac{L^2}{2I} \tag{3.58}$$

where ω is the angular velocity, I, the moment of inertia about an axis passing through the centre of gravity and normal to the line through the masses, and L (i.e. ωI), the total angular momentum of rotation. If no forces act on the rotator, we may put $V = 0$ and the hamiltonian may be given by

$$\hat{H} = \frac{\hat{L}^2}{2I} \tag{3.59}$$

To solve this problem it is most convenient to use the expression of $\hat{L}^2$ in spherical polar coordinates (see Eqs. 2.49). Therefore, Schrödinger's equation $\hat{H}\psi = E\psi$ may be written as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I}{h^2}E\psi = 0 \qquad (3.60)$$

This equation contains two angular variables θ and ϕ. It is solved once again by the method of separation of variables. We look for a solution of the form

$$\psi = \Theta(\theta)\,\Phi\,(\phi) \qquad (3.61)$$

After making this substitution we may write Eq. (3.60) as

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{8\pi^2 I}{h^2}\sin^2\theta = -\frac{1}{\phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad (3.62)$$

Setting both sides of Eq. (3.62) equal to a constant, say m^2, we obtain the pair of differential equations, each in one variable, as

$$\frac{\partial^2\Phi}{\partial\phi^2} + m^2\Phi = 0 \qquad (3.63)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad (3.64)$$

where

$$\beta = \frac{8\pi^2 I}{h^2}E \qquad (3.65)$$

Equation (3.63) has the solution

$$\Phi(\phi) = C\cdot\exp\,(\pm im\phi) \qquad (3.66)$$

This is an acceptable wave function provided m is an integer (see eigenvalues of L_z, Sec. 2.2). This condition arises because Φ is required to be single valued. Thus

$$\Phi(\phi) = \Phi(2\pi + \phi)$$

or

$$\exp\,(im\phi) = \exp\,[im(\phi + 2\pi)] \qquad (3.67)$$

This requires $\exp\,(2\pi mi)$ to be unity, in other words

$$\cos 2\pi m + i\sin 2\pi m = 1$$

This is true if $m = 0, \pm 1, \pm 2, \pm 3, \ldots$ etc. The normalisation condition gives C the value $(2\pi)^{-1/2}$. The normalised solutions of Eq. (3.63) are

$$\Phi_{\pm m}(\phi) = \frac{1}{\sqrt{2\pi}}\exp\,(\pm im\phi) \qquad (3.68)$$

$$(m = 0, 1, 2, 3, \ldots)$$

Equation (3.64) is identical with Eq. (A3.9) of the Appendix 3 when β is replaced by $l(l+1)$. Therefore, Eq. (3.64) has as its solutions the associated

Legendre polynomials $P_l^{|m|}(\cos\theta)$ where 'l' is either zero or a positive integer and further $l \geqslant |m|$. The normalised solutions are given by

$$\Theta(\theta) = \Theta_{l,\pm m}(\theta) = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}}\, P_l^{|m|}(\cos\theta) \tag{3.69}$$

The restriction on 'l' leads to quantisation of the kinetic energy of rotation, whose values are given by

$$E = \frac{l(l+1)h^2}{8\pi^2 I} \tag{3.70}$$

Equation (3.70) is obtained from Eq. (3.65) by substituting $l(l+1)$ for β. The total wave function of a rigid rotator is then given by

$$\psi(\theta, \phi) = \Theta_{l,\pm m}(\theta)\, \Phi_{\pm m}(\phi) = Y_{l,\pm m}(\theta, \phi) \tag{3.71}$$

The functions $Y_l \pm m$ are called spherical harmonics. The following are a few spherical harmonics (see Appendix 3).

$$Y_{0,0} = \frac{1}{2\sqrt{\pi}};\; Y_{1\pm 1} = \frac{\sqrt{3}}{2\sqrt{2\pi}} \sin\theta \exp(\pm i\phi);$$

$$Y_{1,0} = \frac{\sqrt{3}}{2\sqrt{\pi}} \cos\theta;\; Y_{2,0} = \frac{\sqrt{5}}{4\sqrt{\pi}} (3\cos^2\theta - 1);$$

$$Y_{2,\pm 1} = \frac{\sqrt{15}}{4\sqrt{2\pi}} \sin 2\theta \exp(\pm i\phi);$$

$$Y_{2,\pm 2} = \frac{\sqrt{15}}{4\sqrt{2\pi}} \sin^2\theta \exp(\pm 2i\phi) \tag{3.72}$$

It is to be noted from Eq. (3.70) that the energy of a rotator does not depend on the quantum number m. Moreover, the lowest state (for which $l = 0$ and obviously $m = 0$) has zero energy and this is permissible according to the uncertainty principle because there is no variation in wave function, $Y_{0,0}$, on the surface of sphere.

Since the hamiltonian operator of a rigid rotator is given by $\hat{L}^2/2I$ (see Eq. 3.59) and has the eigenvalues $l(l+1)\,h^2/8\pi^2 I$ as shown in Eq. (3.70), the functions $Y_{l\pm m}(\theta, \phi)$ are also the eigenfunctions of the angular momentum operator $\hat{L}^2$. The eigenvalue equation then is given by

$$\hat{L}^2 Y_{l\pm m}(\theta, \phi) = \frac{l(l+1)}{4\pi^2}\, h^2 Y_{l,\pm m}(\theta, \phi) \tag{3.73}$$

Since $\hat{L}^2$ and $\hat{L}_z$ commute, the eigenfunctions of both operators can be chosen to be the same. Thus

$$\begin{aligned}\hat{L}_z\, Y_{l\pm m}(\theta, \phi) &= \frac{h}{2\pi i}\frac{\partial}{\partial\phi}\left[\Theta(\theta)\frac{1}{\sqrt{2\pi}}\exp(\pm im\phi)\right] \\ &= \pm\frac{mh}{2\pi}\left[\Theta(\theta)\frac{1}{\sqrt{2\pi}}\exp(\pm im\phi)\right] = \pm\frac{mh}{2\pi} Y_{l,\pm m}(\theta, \phi)\end{aligned} \tag{3.74}$$

For a given value of l, m can take $(2l + 1)$ integral values $l, l - 1, \ldots, 0 \ldots -(l - 1), -l$. We have seen, therefore, that the solution of the problem of the rigid rotator gives us directly the solution of the angular momentum operators.

3.10 Systems with Discontinuity in the Potential Field

Let us consider an electron (or any particle) of mass m_e moving in one dimension in the direction of positive x-axis in a potential field defined by (Fig. 3.7)

$$V = 0 \quad \text{for} \quad x < 0$$

$$V = V_0 \ \text{for} \quad x > 0$$

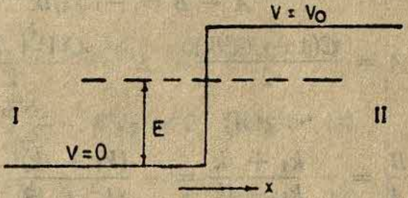

Fig. 3.7 *A simple potential barrier*

The Schrödinger equations for regions I and II are respectively

$$\frac{\partial^2\psi_1}{\partial x^2} + \frac{8\pi^2 m_e}{h^2} E\psi_1 = 0 \tag{3.75}$$

$$\frac{\partial^2\psi_2}{\partial x^2} + \frac{8\pi^2 m_e}{h^2} (E - V_0)\psi_2 = 0 \tag{3.76}$$

where ψ_1 and ψ_2 are the wave functions of the particle in regions I and II respectively. Suppose, the energy is such that $0 < E < V_0$, and let

$$k^2 = \frac{8\pi^2 m_e}{h^2} E; \qquad k_1^2 = \frac{8\pi^2 m_e}{h^2}(V_0 - E) \tag{3.77}$$

The appropriate wave functions for the two regions will clearly follow from Eqs. (3.75) and (3.76). Equation (3.75) has the solution:

$$\psi_1 = A \exp(ikx) + B \exp(-ikx) \tag{3.78}$$

where A and B are arbitrary constants.
Equation (3.76) has the solution:

$$\psi_2 = C \exp(-k_1 x) + D \exp(+k_1 x)$$

where the constant D has to be set equal to zero because ψ_2 must vanish at infinity. Thus

$$\psi_2 = C \exp(-k_1 x) \tag{3.79}$$

where C is another arbitrary constant. In (3.78) the first term, i.e. exp (ikx) is an eigenfunction of the linear momentum operator $(h/2\pi i \cdot \partial/\partial x)$ with the eigenvalue, $kh/2\pi$, while the second term exp $(-ikx)$ has the eigenvalue $-kh/2\pi$. This suggests that the first term represents a wave travelling in the positive x-direction, i.e. the incident beam, and the second term represents a wave travelling in the negative X-direction, i.e. the reflected beam. Both the functions ψ and $\partial\psi/\partial x$ are continuous and the boundary conditions are therefore

$$\psi_1 = \psi_2 \quad \text{and} \quad \frac{\partial\psi_1}{\partial x} = \frac{\partial\psi_2}{\partial x} \quad \text{at} \quad x = 0$$

which give the following equations

$$A + B = C \tag{3.80}$$

$$A - B = -Ck_1/ik \tag{3.81}$$

or

$$A = \frac{C(1 - k_1/ik)}{2}; \quad B = \frac{C(1 + k_1/ik)}{2} \tag{3.82}$$

Therefore,

$$\frac{B}{A} = -\frac{k_1 + ik}{k_1 - ik} = -\frac{(k_1 + ik)^2}{k_1^2 + k^2} = \alpha \tag{3.83}$$

The intensities of the reflected and the incident beam are in the ratio $|B|^2 : |A|^2$, but from Eq. (3.83) $|\alpha|^2 = \alpha\alpha^* = 1$. Hence, the intensity of the reflected beam equals that of the incident beam. That the wave-function in Eq. (3.79) in the region II decays exponentially is indicative of the particles suffering almost total reflection in the region I.

However, there is a small but finite probability of particles being transmitted in the region II, which is not predictable from the classical mechanics. We define the transmission coefficients by $|C/A|^2$ and it follows from Eq. (3.82) that

$$\left|\frac{C}{A}\right|^2 = \frac{2ik}{ik - k_1}\,\frac{2ik}{ik + k_1} = \frac{4k^2}{k_1^2 + k}$$

Substituting for k_1 and k (see Eq. 3.77)

$$\left|\frac{C}{A}\right|^2 = \frac{4E}{V_0} \neq 0 \tag{3.84}$$

The transmission coefficient is not zero unless the potential energy of the barrier is infinite. A study of more complicated barriers such as that depicted in Fig. 3.8 reveals a striking feature, known as the 'tunnel effect'. Consider a beam of electrons moving in a potential field defined as

$$V = 0 \quad \text{for} \quad x < a$$

$$V = V_0 \quad \text{for} \quad a < x < b$$

$$V = 0 \quad \text{for} \quad x > b$$

with $E < V_0$

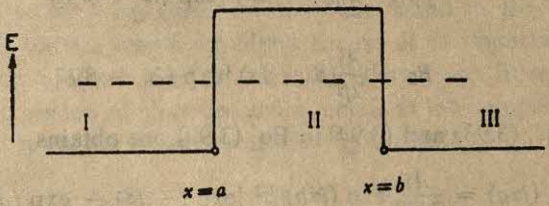

Fig. 3.8 *A potential barrier with a finite thickness*

If we define

$$\alpha^2 = \frac{8\pi^2 m_e E}{h^2}, \quad \beta^2 = \frac{8\pi^2 m_e}{h^2}(V_0 - E) \tag{3.85}$$

then Schrödinger equations for the three regions are as follows:

$$\left.\begin{aligned} &\frac{\partial^2\psi_1}{\partial x^2} + \alpha^2\psi_1 = 0 \quad \text{(Region I)} \\ &\frac{\partial^2\psi_2}{\partial x^2} - \beta^2\psi_2 = 0 \quad \text{(Region II)} \\ &\frac{\partial^3\psi_3}{\partial x^2} + \alpha^2\psi_3 = 0 \quad \text{(Region III)} \end{aligned}\right\} \tag{3.86}$$

The wave functions for the three regions are

$$\left.\begin{aligned} \psi_1 &= A_1 \exp(i\alpha x) + A_2 \exp(-i\alpha x) \\ \psi_2 &= B_1 \exp(+\beta x) + B_2 \exp(-\beta x) \\ \psi_3 &= A_1' \exp(i\alpha x) + A_2' \exp(-i\alpha x) \end{aligned}\right\} \tag{3.87}$$

Since in region III there is nothing to cause reflection of the electron, $A_2' = 0$. Since the potential energy is either finite or zero, $\frac{\partial^2\psi}{\partial x^2}$ according to the wave equation is finite. So there cannot be any sudden change of $\partial\psi/\partial x$. In other words $\partial\psi/\partial x$ must be continuous, in addition to ψ being continuous. The continuity conditions for ψ and $\partial\psi/\partial x$ at $x = a$ (i.e. $\psi_1 = \psi_2$ and $\partial\psi_1/\partial x = \partial\psi_2/\partial x$ at $x = a$) lead to the following equations:

$$A_1 \exp(i\alpha a) + A_2 \exp(-i\alpha a) = B_1 \exp(\beta a) + B_2 \exp(-\beta a) \tag{3.88}$$

$$A_1 \exp(i\alpha a) - A_2 \exp(-i\alpha a) = \frac{\beta}{i\alpha}[B_1 \exp(\beta a) - B_2 \exp(-\beta a)] \tag{3.89}$$

$$2A_1 \exp(i\alpha a) = B_1 \exp(\beta a)(1 + \beta/i\alpha) + B_2 \exp(-\beta a)(1 - \beta/i\alpha) \tag{3.90}$$

The continuity conditions for ψ and $\partial\psi/\partial x$ at $x = b$ give rise to the following equations:

$$B_1 \exp(\beta b) + B_2 \exp(-\beta b) = A_1' \exp(i\alpha b) \tag{3.91}$$

$$B_1 \exp(\beta b) - B_2 \exp(-\beta b) = \frac{i\alpha}{\beta}A_1' \exp(i\alpha b) \tag{3.92}$$

or
$$B_1 = \frac{A_1'}{2\beta}(\beta + i\alpha)\,[\exp\,(i\alpha - \beta)b] \tag{3.93}$$

$$B_2 = \frac{A_1'}{2\beta}(\beta - i\alpha)\,[\exp\,(i\alpha + \beta)b] \tag{3.94}$$

Inserting Eqs. (3.93) and (3.94) in Eq. (3.90) one obtains

$$\begin{aligned} 2A_1 \exp\,(i\alpha a) = \frac{A_1}{2i\alpha\beta} \exp\,(i\alpha b)[\beta^2\,\{\exp\,(-d\beta) - \exp\,(d\beta)\} \\ +\alpha^2\,\{\exp\,(d\beta) - \exp\,(-d\beta)\} + 2i\alpha\beta\,\{\exp\,(d\beta) \\ -\exp\,(-d\beta)\}] \end{aligned} \tag{3.95}$$

where d is written for $(b - a)$ which determines the thickness of the potential barrier. Since

$$\exp\,(\theta) + \exp\,(-\theta) = 2\cosh\theta$$
$$\exp\,(\theta) - \exp\,(-\theta) = 2\sinh\theta$$

We may write Eq. (3.95) as

$$A_1 = \frac{A'\exp\,(i\alpha d)}{4i\alpha\beta}[2(\alpha^2 - \beta^2)\sinh\,(d\beta) + 4i\alpha\beta\cosh\,(d\beta)] \tag{3.96}$$

$$\frac{A_1'}{A_1} = \frac{\exp\,(-i\alpha d)}{\left[\dfrac{(\alpha^2 - \beta^2)\sinh\,(\alpha\beta)}{2i\alpha\beta} + \cosh\,(d\beta)\right]} \tag{3.97}$$

The transmission coefficient $\left|\dfrac{A_1'}{A_1}\right|^2$ is, therefore, given by

$$\begin{aligned} \left|\frac{A_1'}{A_1}\right|^2 &= \frac{\exp\,(i\alpha d)\exp\,(-i\alpha d)}{\left[\dfrac{(\alpha^2 - \beta^2)\sinh\,(d\beta)}{2i\alpha\beta} + \cosh\,(d\beta)\right]\left[\cosh\,(d\beta) - \dfrac{(\alpha^2 - \beta^2)\sinh\,(d\beta)}{2i\alpha\beta}\right]} \\ &= \frac{1}{\cosh^2(\beta d) + \dfrac{(\alpha^2 - \beta^2)^2\sinh^2(\beta d)}{4\alpha^2\beta^2}} \end{aligned} \tag{3.98}$$

For very large value of βd, both cosh (βd) and sinh (βd) becomes $\frac{1}{2}\exp\,(\beta d)$ and Eq. (3.98) may be reduced to

$$\left|\frac{A_1'}{A_1}\right|^2 = \frac{16\alpha^2\beta^2\exp\,(-2\beta d)}{(\alpha^2 + \beta^2)^2} \tag{3.99}$$

showing that A_1' is generally non-zero and there is a finite probability of the particle tunnelling through this potential barrier. This equation shows that the transmission coefficient diminishes exponentially as the thickness of the barrier increases. It also shows how the transmission coefficient depends on the potential energy of the barrier and mass of the particle through α and β. This result that the particles are able to tunnel through the barrier although their kinetic energy is not great enough to allow them to pass it cannot be predicted from the classical mechanics.

There is enough evidence to demonstrate that the tunnelling phenomena occur in nature. The most direct evidence is found in the radioactive disintegration of atomic nuclei by alpha decay. It is important in many chemical processes in which electron transfer takes place from one atom to another. The emission of electrons from metals at low temperatures and high electric field strengths is also controlled by tunnelling.

3.11 Rotation of Molecules

Rotation of a molecule can be treated, to a good approximation, as rotation of a rigid body for which one can find a Cartesian coordinate system. We shall first define the moment of inertia of a rigid body. The moment of inertia is a tensor and defined in a Cartesian coordinate system as

$$I_{ij} = \sum_{\alpha} m_\alpha (r_\alpha^2 \delta_{ij} - x_{\alpha,i} \cdot x_{\alpha,j}) \tag{3.100}$$

where m_α is the mass of the particle α in a molecule, r_α is the distance of α from the centre of mass, $x_{\alpha,i}$, $x_{\alpha,j}$ and $x_{\alpha,k}$ are the x, y and z coordinates of the particle α (see Appendix 3B). Thus, from Eq. (3.100) one may write

$$\begin{aligned} I_{xx} &= \sum_{\alpha} m_\alpha (r_\alpha^2 - x_\alpha^2) = \sum_{\alpha} m_\alpha (x_\alpha^2 + y_\alpha^2 + z_\alpha^2 - x_\alpha^2) \\ &= \sum_{\alpha} m_\alpha (y_\alpha^2 + z_\alpha^2) \\ I_{yy} &= \sum_{\alpha} m_\alpha (x_\alpha^2 + z_\alpha^2) \\ I_{zz} &= \sum_{\alpha} m_\alpha (x_\alpha^2 + y_\alpha^2) \end{aligned} \tag{3.101}$$

where each sum is taken over all the atoms in the molecule. Since the matrix I_{ij} (i.e., I_{xy}, I_{yz}, etc.) can be shown to be symmetric and real, the matrix I_{ij} is diagonalised. The eigenvalues are called the principal moments of inertia and have the form given by Eq. (3.101). Its eigenvectors are called the principal axes. The kinetic energy of rotation of a rigid body is then determined by the moment of inertia I_{ii} about the axis of rotation, i, and the angular velocity ω_i about the axis i ($i = x, y, z$) [see Eq. 3.58].

$$E_{\text{rot}} = \tfrac{1}{2} I_{ii} \omega_i^2 = \frac{L_{ii}^2}{2I_{ii}} \tag{3.102}$$

If rotation about all three axes is allowed, the total kinetic energy is given by

$$E_{\text{rot}} = \frac{L_x^2}{2I_{xx}} + \frac{L_y^2}{2I_{yy}} + \frac{L_z^2}{2I_{zz}} \tag{3.103}$$

where L_x, L_y and L_z are the three components of angular momentum. Equation (3.103) is the key equation which can be used to break the discussion according to the type of molecules being considered.

Case (I): $I = I_{xx} = I_{yy} = I_{zz}$

Such a system is known as spherical top. Symmetry of this type is found in molecules like CH_4, CCl_4, SF_6, etc. For such systems the rotational energy levels are given by Eq. (3.70) and the corresponding wavefunctions are the spherical harmonics (Eq. 3.71).

Case (*2*): $I = I_{xx} = I_{yy} \neq I_{zz}$

Such a system is called the symmetric top. Symmetry of this type is found in all diatomic and linear polyatomic molecules, NH_3, benzene, etc. For linear molecules the internuclear axis is used as the z-axis. For molecules like NH_3 (pyramidal), the axis of three-fold symmetry can be used as the z-axis. The rotational energy of a symmetric top is given by

$$\begin{aligned} E_{\text{rot}} &= \frac{L_x^2 + L_y^2}{2I} + \frac{L_z^2}{2I_{zz}} \\ &= \frac{L_x^2 + L_y^2 + L_z^2}{2I} + \frac{L_z^2}{2}\left[\frac{1}{I_{zz}} - \frac{1}{I}\right] \\ &= \frac{L^2}{2I} + \frac{L_z^2}{2}\left[\frac{1}{I_{zz}} - \frac{1}{I}\right] \qquad (3.104) \end{aligned}$$

Replacing L^2 and L_z^2 by their quantum mechanical operators we have

$$\hat{H}_{\text{rot}} = \frac{\hat{L}^2}{2I} + \frac{\hat{L}_z^2}{2I}\left[\frac{1}{I_{zz}} - \frac{1}{I}\right] \qquad (3.105)$$

We then apply the eigenvalue equations [Eqs (3.73) and (3.74)] to Eq. (3.105)

$$\begin{aligned} \hat{H}_{\text{rot}}\, Y_{l,\pm m}(\theta, \phi) &= \frac{1}{2I}\hat{L}^2 Y_{l,\pm m}(\theta, \phi) + \tfrac{1}{2}\left[\frac{1}{I_{zz}} - \frac{1}{I}\right]\hat{L}_z^2 Y_{l,\pm m}(\theta, \phi) \\ &= E_{\text{rot}} Y_{l,\pm m}(\theta, \phi) \qquad (3.106) \end{aligned}$$

where

$$E_{\text{rot}} = \frac{h^2}{8\pi^2}\left[\frac{l(l+1)}{I} + m^2\left(\frac{1}{I_{zz}} - \frac{1}{I}\right)\right] \qquad (3.107)$$

with $l = 0, 1, 2, \ldots$

$m = 0, \pm 1, \pm 2, \ldots$

Above equations show that while wavefunctions of the spherical top and symmetric top are given by the same spherical harmonics, the energy levels of the symmetric top, unlike the spherical top, depend on m, i.e., on the projection of the angular momentum vector on the z-axis. Each energy level is therefore doubly degenerate because $+m$ and $-m$ lead to same energy. Unlike the spherical top where each level is $(2l + 1)$ fold degenerate, the $+m$ and $-m$ correspond to clockwise and anticlockwise rotations about the z-axis, respectively. When $m = 0$, it means there is no component of the angular momentum about the z-axis. This is possible if the angular momentum vector $\vec{\mathbf{L}}$ is perpendicular to the z-axis. In the case of a diatomic molecule, AB, $m = 0$ corresponds to the end-over-end rotation, i.e., the molecule rotates about an axis perpendicular to the z-axis (Fig. 3.9). Since there are two such axes (x and y), the molecule AB will have two degrees of rotational freedom.

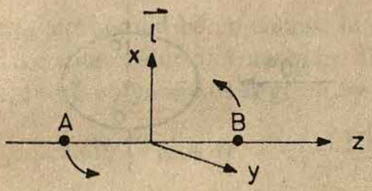

Fig. 3.9 *End-over-end rotation of a diatomic molecule*

When $m = \pm l$ there is a large component of angular momentum vector on the z-axis and the molecule rotation is almost about the z-axis as shown in Fig. 3.10. If the molecule AB is imagined to be a cylinder, then the cylinder rotates about its axis when $m = \pm l$. In real molecules the only rotation about the z-axis is rotation of each atom about its own nucleus. Thus a diatomic or any linear polyatomic molecule has only two degrees of rotational freedom.

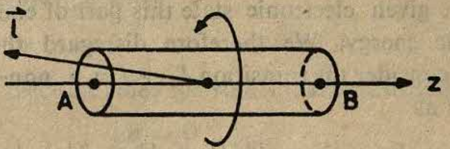

Fig. 3.10 *Rotation of a molecule about the bond axis*

Case (3): $I_{xx} \neq I_{yy} \neq I_{zz}$

Such a system is called the asymmetric top—a molecule in which all three moments of inertia are different. Molecules like H_2O, SO_2, etc. belong to this category. In the asymmetric top there is no axis around which angular momentum is conserved. Although there are still $(2l + 1)$ levels for each value of l the levels are not degenerate and the wavefunctions are not spherical harmonics[1].

3.12 Rotational Spectra

When a dipole rotates in a plane perpendicular to the axis of the dipole, an observer also in the plane of rotation will see the fluctuating dipole (Fig. 3.11). The fluctuating dipole can interact with the electromagnetic field of radiation. Therefore, molecules with permanent dipole moment can emit or absorb radiation by making a transition between different energy levels of rotation. According to classical theory one should observe radiations of continuous frequencies. But the rotational spectra of molecules consist of discrete lines which are observed in the far-infrared or microwave region.

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[1] G.W. King, R. Hainer and P.C. Cross, J. Chem. Phys., **11**, 27, (1943); **12**, 210, (1944); **15**, 820, (1947); **17**, 826, (1949).

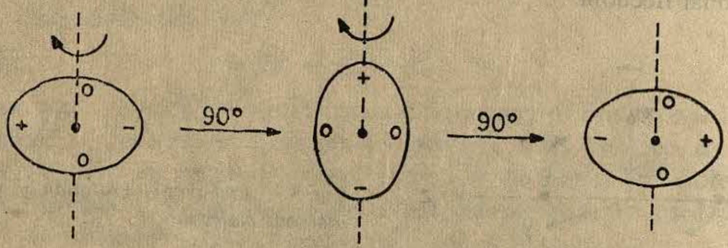

Fig. 3.11 *The +, −, and 0 refer to the positive, negative and zero charge. The dashed line is the axis of rotation*

The energy of rotation of a diatomic molecule is given by Eq. (3.107). In a diatomic or any linear polyatomic molecule, the only contribution to I_{zz} arises from electrons and from the non-zero radii of the nuclei. Both are very small compared to I. The energy term associated with L_z^2 is therefore either very large when $L_z \neq 0$ for electrons or very small when $L_z = 0$ for electrons. For a given electronic state this part of energy can be included in the electronic energy. We therefore disregard the second term of Eq. (3.107) and consider the transition $l' \rightarrow l$ in a non-vibrating molecule. ΔE is then given as

$$\Delta E = E_{l'} - E_l = B[l'(l'+1) - l(l+1)] \tag{3.108}$$

where

$$B = \frac{h^2}{8\pi^2 I} \tag{3.109}$$

If μ_0 be the permanent dipole moment of the diatomic molecule, it has three components in spherical polar coordinates as [see Appendix 2]

$$\begin{aligned} \mu_z &= \mu_0 \cos\theta \\ \mu_x &= \mu_0 \sin\theta \cos\phi \\ \mu_y &= \mu_0 \sin\theta \sin\phi \end{aligned} \tag{3.110}$$

We consider the z-component of the dipole moment of transition. Each rotational state is characterised by two quantum numbers l and m [see Eq. 3.71]. Then the z-component of the transition dipole is given as

$$R_z = \mu_0 \iint Y_{l'\pm m'}(\theta, \phi) \cos\theta\, Y_{l\pm m}(\theta, \phi) \sin\theta\, d\theta\, d\phi \tag{3.111}$$

Writing the functions in terms of the associated Legendre polynomials one obtains

$$R_z = \mu_0 N_{l',m'} N_{l,m} \int_0^{\pi} P_{l'}^{(m')}(\cos\theta), \cos\theta \cdot P_l^{(m)}(\cos\theta) \sin\theta\, d\theta$$

$$\int_0^{2\pi} \exp[i(m'-m)\phi]\, d\phi \tag{3.112}$$

where $N_{l',m'}$, $N_{l,m}$ are the normalising factors given in Eq. (3.69). In Eq. (3.112) the integral over $\exp[i(m' - m)\phi]$ vanishes unless $|m| = |m'|$. Thus, for the rotational transition to be observed

$$\Delta m = 0 \tag{3.113}$$

i.e., there should be no change in angular momentum along the main axis of the rotator during transition. The recurrence relation for the Associated Legendre polynomials is given by

$$\cos\theta P_l^{|m|}(\cos\theta) = \frac{l+|m|}{2l+1}P_{l-1}^{|m|}(\cos\theta) + \frac{l-|m|+1}{2l+1}P_{l+1}^{|m|}(\cos\theta) \tag{3.114}$$

Substituting Eq. (3.114) for the integral over θ in Eq. (3.112), we have

$$\int_0^{\pi}\left[P_l^{|m'|}(\cos\theta)\cdot\frac{l+|m|}{2l+1}P_{l-1}^{|m|}(\cos\theta)\right.$$
$$\left. + P_l^{|m'|}(\cos\theta)\,\frac{l-|m|+1}{2l+1}P_{l+1}^{|m|}(\cos\theta)\right]\sin\theta\,d\theta \tag{3.115}$$

This integral is nonvanishing when

$$l' = l - 1 \qquad \text{or} \qquad l' = l + 1$$

In other words, the selection rules for rotational transitions are

$$\begin{aligned}\Delta m &= 0\\ \Delta l &= \pm 1\end{aligned} \tag{3.116}$$

and $$\mu_0 \neq 0$$

The energy of the transition $l + 1 \to l$ can therefore be expressed as

$$\begin{aligned}\Delta E &= B[(l+1)(l+2) - l(l+1)]\\ &= 2B(l+1)\end{aligned} \tag{3.117}$$

Thus, we find that the rotational spectrum consists of discrete lines of frequencies $2B/h$, $4B/h$, $6B/h$, etc. (Fig. 3.12) with separation of $2B$ between the successive lines. By measuring the spacing between the lines one obtains B, hence the moment of inertia and the internuclear distance. Typical values of B are in the range 1–10 cm^{-1}. For example, for HCl, $B = 10.6$ cm^{-1}; HI, $B = 6.5$ cm^{-1}; and NaCl, $B = 0.2$ cm^{-1}. Thus the rotational spectra of heavier molecules appear in the microwave region. The spherically symmetric molecules do not have any permanent dipole moment. The pure rotation spectrum of such molecules cannot be observed.

We have so far assumed that the internuclear distance in a rotating molecule is fixed. This is questionable because the molecule is always vibrating. When the vibrational quantum number is high, because of the asymmetry of the potential energy curve the average value of R (i.e., the inter-nuclear distance in a bond) increases and the moment of inertia increases. Besides, there is a possibility of stretching of the bond by centrifugal force during rotation. Both effects lead to somewhat lower values of the rotational energies, and thus reduce the separation between the two successive lines in the rotational spectra.

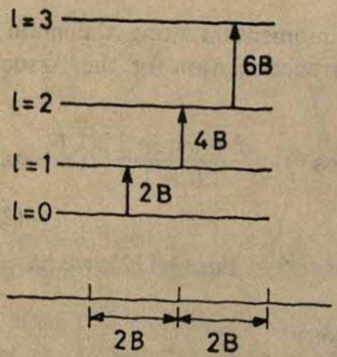

Fig. 3.12 *Rotational spectra with discrete lines separated by 2B*

APPENDIX 3A

Consider a function

$$Y = (1 - x^2)^l \tag{A3.1}$$

Then

$$\frac{dY}{dx} = -2xl(1 - x^2)^{l-1} = -\frac{2xl}{(1 - x^2)}Y$$

or

$$(1 - x^2)\frac{dY}{dx} + 2lxY = 0 \tag{A3.2}$$

Differentiating this equation $(m + l + 1)$ times, using the Leibnitz theorem and rearranging, we obtain,

$$(1 - x^2)\frac{d^2Z}{dx^2} - 2x(m + 1)\frac{dZ}{dx} + (m + l + 1)(l - m)Z = 0 \tag{A3.3}$$

where

$$Z = C\frac{d^{m+l}}{dx^{m+l}}Y = C\frac{d^m}{dx^m}\frac{d^l}{dx^l}Y = \frac{d^m}{dx^m}P_l(x) \tag{A3.4}$$

and

$$P_l(x) = C\frac{d^l}{dx^l}(1 - x^2)^l = \frac{1}{2^l l!}\frac{d^l}{dx^l}(1 - x^2)^l \tag{A3.5}$$

The particular function $P_l(x)$, defined in (A3.5), is called Legendre's polynomial of degree l.

Let us assume a function

$$Z = U(1 - x^2)^{-|m|/2} (m\text{, a positive integer}) \tag{A3.6}$$

Inserting this function into Eq. (A3.3) we obtain a differential equation

$$(1 - x^2)\frac{d^2U}{dx^2} - 2x\frac{dU}{dx} + \left[l(l + 1) - \frac{m^2}{1 - x^2}\right]U = 0 \tag{A3.7}$$

This equation is known as Associated Legendre equation and the function U usually written as $P_l^m(x)$ is called the Associated Legendre polynomial of degree l and order $m(l \geqslant |m|)$. Thus

$$P_l^{|m|}(x) = (1 - x^2)^{|m|/2} Z = (1 - x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \qquad \text{(A3.8)}$$

When we write $x = \cos\theta$, Eq. (A3.7) becomes

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dU}{d\theta}\right) + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]U = 0 \qquad \text{(A3.9)}$$

and the solution of this equation becomes

$$U = P_l^{|m|}(\cos\theta) = \sin^{|m|}\theta \frac{d^{|m|}}{d(\cos\theta)^{|m|}} P_l(\cos\theta) \qquad \text{(A3.10)}$$

In the following we work out for a few values of l and m the Associated Legendre functions in x.

$$\left.\begin{aligned}
P_0^0(x) &= P_0(x) = 1 \\
P_1^0(x) &= P_1(x) = \tfrac{1}{2}(-2x) = -x \\
P_1^1(x) &= (1 - x^2)^{1/2}\frac{d}{dx}P_1(x) = -(1 - x^2)^{1/2} \\
P_2^0(x) &= P_2(x) = \tfrac{1}{8}\cdot\frac{d^2}{dx^2}(1 - x^2)^2 = \tfrac{1}{2}(3x^2 - 1) \\
P_2^1(x) &= (1 - x^2)^{1/2}\frac{d}{dx}P_2(x) = (1 - x^2)^{1/2}3x \\
P_2^2(x) &= (1 - x^2)\frac{d^2}{dx^2}P_2(x) = 3(1 - x)^2
\end{aligned}\right\} \qquad \text{(A3.11)}$$

APPENDIX 3B

In this section we shall outline the concept of tensors. When a vector, say velocity, $\mathbf{v}$ of a particle moving in a particular direction is multiplied by a scalar K such that

$$\mathbf{v}_1 = K\mathbf{v}$$

The new velocity $\mathbf{v}_1$ has a different magnitude but refers to the same direction of $\mathbf{v}$. If the medium in which the particle is moving is not isotropic it is necessary to replace the scalar K by a more general mathematical device that can change the direction of the vector as well as its magnitude. Such a device is called tensor. For example, if an electric field $\mathbf{E}$ is applied to a molecule along any axis of the molecule, a dipole moment can be induced perpendicular to the direction of the applied field. This can be expressed as

$$\boldsymbol{\mu}_{\text{ind}} = \alpha\mathbf{E}$$

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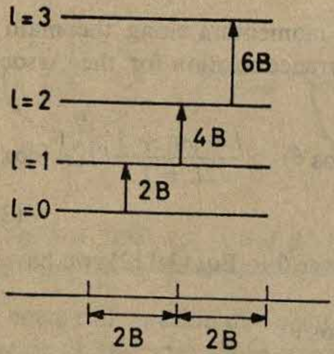

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$$\boldsymbol{\mu}_{\text{ind}} = \alpha\mathbf{E}$$

where α is called the polarizability tensor of the molecule. Similarly, an angular momentum vector **L** can be generated in a direction perpendicular to the plane of rotation of a moving particle with angular velocity $\boldsymbol{\omega}$ and this can be expressed as $\mathbf{L} = I\boldsymbol{\omega}$ where I is the moment-of-inertia tensor. Tensors like α, I, etc., can have more than three components in a system of rectangular axes. A vector has three components and may also be called a tensor of first rank.

We shall first consider the background for the definition of a tensor of second rank. Consider any two systems of rectangular axes with common origin as shown in Fig. (3B.1). The equations of coordinate transformation can be written as

$$\begin{bmatrix} x_1' \\ x_2' \\ x_3' \end{bmatrix} = \begin{bmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \tag{B.1}$$

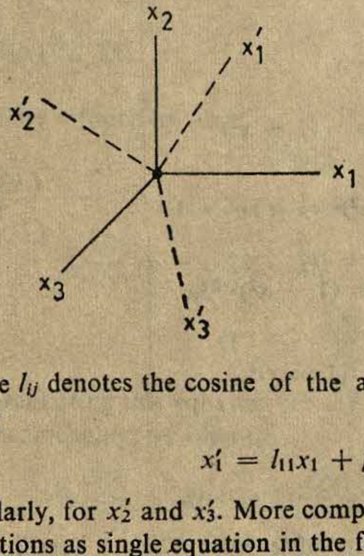

Fig. 3B.1 *Two systems of rectangular axes with common origin*

where l_{ij} denotes the cosine of the angle between ox_i and ox_j'. One may write

$$x_1' = l_{11}x_1 + l_{12}x_2 + l_{13}x_3$$

Similarly, for x_2' and x_3'. More compactly, one can write the whole set of equations as single equation in the form

$$x_j' = l_{ji}x_i \qquad i = 1, 2, 3 \qquad j = 1, 2, 3 \tag{B.2}$$

where the summation over the repeated index, i, on the right hand side of Eq. (B.2) is implied. Let us now consider two entities, a_i and b_j in one system of axes and a_p' and b_q' are the components of the same in the other system of axes. One can write using the convention of Eq. (B.2)

$$a_p' = l_{pi}a_i \qquad b_q' = l_{qj}b_j \tag{B.3}$$

where l_{pi} and l_{qj} have the usual meanings.

We consider now the product $a'_p\, b'_q$ which is given by

$$\begin{aligned} a'_p\, b'_q &= l_{pi}a_i l_{qj} b_j \\ &= l_{pi} l_{qj} a_i b_j \end{aligned} \tag{B.4}$$

One can now visualise that the right hand side of (B.4) has nine terms obtained by giving the suffixes i and j all possible pairs of values ($i = 1, 2, 3$; $j = 1, 2, 3$). We now see that an entity can be represented by a two-suffix set. If one such entity is denoted by A'_{pq} in one system of axes and by A_{ij} in the other system of axes, they are connected by the relation

$$A'_{pq} = l_{pi} l_{qj} A_{ij} \tag{B.5}$$

Such an entity is called a tensor of second rank. In fact one can think of an entity representable by more than two suffixes and develop its algebra.

We introduce a symbol ϵ_{ijk} which can be used to simplify equations. If i, j, k is an even permutation of x_1, x_2 and x_3 (or x, y and z) then ϵ_{ijk} takes on the value one, while an odd permutation gives ϵ_{ijk} the value minus one.

$$\begin{aligned} \epsilon_{ijk} &= \epsilon_{jki} = \epsilon_{kij} = 1 \\ \epsilon_{ikj} &= \epsilon_{kji} = \epsilon_{jik} = -1 \end{aligned} \tag{B.6}$$

If any pair of the subscripts i, j and k is identical, then

$$\epsilon_{ijk} = 0 \tag{B.7}$$

This symbol ϵ_{ijk} is the unit tensor in three dimensions. One can easily show that Kronecker's delta, δ_{ij} is a tensor in two dimensions or of order two (or second rank).

$$\begin{aligned} \delta_{ij} &= 0 \quad \text{if} \quad i \neq j \\ &= 1 \quad \text{if} \quad i = j \end{aligned} \tag{B.8}$$

For an arbitrary vector $\mathbf{a}_i$, the tensorial character of δ_{ij} is revealed as

$$\mathbf{a}_j = \delta_{ij}\mathbf{a}_i \tag{B.9}$$

where the summation over the repeated index i is implied. We may encounter the product of two Kronecker's deltas having a common subscript, i.e.,

$$\delta_{ij}\delta_{kj} = \delta_{ik} \tag{B.10}$$

This sort of relation is referred to as sum rule. It should be noted that δ_{ii} is not unity but equal to 3 as the sum over i gives

$$\delta_{ii} = \delta_{xx} + \delta_{yy} + \delta_{zz} = 3 \tag{B.11}$$

Here i can be x, y and z or x_1, x_2 and x_3 of Fig. (3B.1).

One can use the symbol ϵ_{ijk} to define the vector product of **a** and **b**. The ith component of the vector product may be written as

$$\begin{aligned} C_i = \epsilon_{ijk}a_j b_k &= \epsilon_{iii}a_i b_i + \epsilon_{iij}a_i b_j + \epsilon_{iik}a_i b_k + \epsilon_{iji}a_j b_i + \epsilon_{ijj}a_j b_j \\ &\quad + \epsilon_{ijk}a_j b_k + \epsilon_{iki}a_k b_i + \epsilon_{ikj}a_k b_j + \epsilon_{ikk}a_k b_k \\ &= \epsilon_{ijk}a_j b_k + \epsilon_{ikj}a_k b_j \\ &= a_j b_k - a_k b_j \end{aligned} \tag{B.12}$$

Similarly, the jth component of the vector $\mathbf{C}$ can be written as

$$C_j = \epsilon_{jki} a_k b_i \tag{B.13}$$

The vector product $\mathbf{C} = \mathbf{a} \times \mathbf{b}$ can also be written in the form of the following determinant.

$$\mathbf{C} = \mathbf{a} \times \mathbf{b}$$

$$= \begin{vmatrix} i & j & k \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix} \tag{B.14}$$

where i, j and k are the components of the unit vector $\mathbf{e}$ on the three axes (Fig. 3B.1). The permutation symbol ϵ_{ijk} can also be expressed as a determinant.

$$\epsilon_{ijk} = \begin{vmatrix} \delta_{ix} & \delta_{iy} & \delta_{iz} \\ \delta_{jx} & \delta_{jy} & \delta_{jz} \\ \delta_{kx} & \delta_{ky} & \delta_{kz} \end{vmatrix} \tag{B.15}$$

One can show that this definition is consistent with Eq. (B.6). If any pair of the subscripts i, j, and k are identical, the determinant is zero and consistent with Eq. (B.7). Using the rule for multiplying two determinants and Eq. (B.10) one obtains

$$\epsilon_{ijk}\epsilon_{lmn} = \begin{vmatrix} \delta_{ix} & \delta_{iy} & \delta_{iz} \\ \delta_{jx} & \delta_{jy} & \delta_{jz} \\ \delta_{kx} & \delta_{ky} & \delta_{kz} \end{vmatrix} \begin{vmatrix} \delta_{lx} & \delta_{ly} & \delta_{lz} \\ \delta_{mx} & \delta_{my} & \delta_{mz} \\ \delta_{nx} & \delta_{ny} & \delta_{nz} \end{vmatrix}$$

$$= \begin{vmatrix} \delta_{il} & \delta_{im} & \delta_{in} \\ \delta_{jl} & \delta_{jm} & \delta_{jn} \\ \delta_{kl} & \delta_{km} & \delta_{kn} \end{vmatrix} \tag{B.16}$$

We now consider the product $\epsilon_{ijk}\,\epsilon_{imn}$ where summation over i is implied. We have

$$\epsilon_{ijk}\epsilon_{imn} = \begin{vmatrix} \delta_{ii} & \delta_{im} & \delta_{in} \\ \delta_{ji} & \delta_{jm} & \delta_{jn} \\ \delta_{ki} & \delta_{km} & \delta_{kn} \end{vmatrix}$$

$$\begin{aligned} &= \delta_{ii}(\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}) - \delta_{im}(\delta_{ji}\delta_{kn} - \delta_{jn}\delta_{ki}) \\ &\quad + \delta_{in}(\delta_{ji}\delta_{km} - \delta_{jm}\delta_{ki}) \\ &= 3(\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}) - (\delta_{mj}\delta_{kn} - \delta_{jn}\delta_{km}) + (\delta_{nj}\delta_{km} - \delta_{jm}\delta_{kn}) \\ &= \delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km} \end{aligned} \tag{B.17}$$

where we recalled that $\delta_{ii} = 3$ and Eq. (B.10).

We now consider the moment of inertia tensor of a rigid body about a line *OM*. In the Fig. (3B.2), *P* is the position of a particle of mass m_α and *PL* is the perpendicular distance of the point *P*, from the line *OM*.

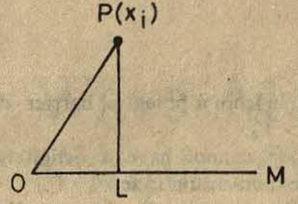

Fig. 3B.2 *Moment of inertia of a rigid body about the line OM*

By definition, the moment of inertia about the line *OM* is

$$\sum_\alpha m_\alpha (PL)^2$$

We assume *O* as the origin of a system of three rectangular axes OX_1, OX_2, and OX_3. Let l_i be the direction cosine of the line *OM*. The direction *OM* can be defined by the unit vector $\mathbf{e} = il_1 + jl_2 + kl_3$. Then the vector **PL** is given as

$$\mathbf{PL} = OP \sin\theta = \mathbf{OP} \times \mathbf{e}$$

or using the property of ϵ_{ijk} one writes

$$\mathbf{PL} = \epsilon_{ijk} l_j x_k \tag{B.18}$$

$$\begin{aligned} PL^2 &= (\epsilon_{ijk} l_j x_k)(\epsilon_{imn} l_m x_n) \\ &= \epsilon_{ijk}\epsilon_{imn} l_j l_m x_k x_n \\ &= (\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}) l_j l_m x_k x_n \quad \text{[using Eq. B.17]} \\ &= (\delta_{jm} l_j l_m)(\delta_{kn} x_k x_n) - (\delta_{jn} l_j x_n)(\delta_{km} l_m x_k) \\ &= l_j l_j (x_k x_k) - (l_n x_n)(l_m x_m) \\ &= x_k x_k - (l_n x_n)(l_m x_m) \quad \text{[because } l_j^2 = 1\text{]} \\ &= x_k x_k l_m \delta_{mn} l_n - l_m x_m l_n x_n \\ &= l_m [x_k x_k \delta_{mn} - x_m x_n] l_n \end{aligned} \tag{B.19}$$

Thus, the moment of inertia of a rigid body about the line *OM* is given as

$$\sum_\alpha m_\alpha l_m \left[x_{\alpha,k} x_{\alpha,k} \delta_{mn} - x_{\alpha,n} x_{\alpha,m} \right] l_n$$

or

$$l_m \left[\sum_\alpha m_\alpha (x_{\alpha.k}^2 \delta_{mn} - x_{\alpha,n} x_{\alpha,m}) \right] l_n$$

where $x_{\alpha,m}$, $x_{\alpha,n}$ are the coordinates of the particle α. We write

$$I_{mn} = \sum_\alpha m_\alpha (r_\alpha^2 \delta_{mn} - x_{\alpha,m} x_{\alpha,n}) \tag{B.20}$$

and the moment of inertia about a given line with direction cosines l_m is $l_m I_{mn} l_n$.

Clearly, I_{mn} is a symmetric tensor of second rank independent of the direction cosines of the line *OM* and depends on the configuration of the system relative to the point *O* in Fig. (3B.1).

PROBLEMS

1. Determine the reflection coefficient of a particle from a potential barrier described in Fig. 3.7 with the energy of the particle $E > V_0$.
2. Show that a particle in a one-dimensional box cannot have a definitely known momentum and that the average value of the momentum is zero.
3. Find the lowest kinetic energy of an electron in a rectangular box of dimensions 1×10^{-13} cm, 1.5×10^{-13} cm and 2×10^{-13} cm.
4. Show that the quantum mechanical mean value of the square of the positional co-ordinate of an electron in-a-box agrees with the classical results when the system is in highly excited quantum states.
5. Using angular coordinates, obtain the solutions of the Schrödinger equation for an electron moving on a circular ring of radius r in a constant zero potential.
6. Obtain the first few rotational energy levels of HBr and point out the degree of degeneracy of each level. Calculate its lowest transition energy in Å. [Use Eq. (3.70) for this problem].
7. Find the moment of inertia tensor for H_2O (nonlinear) and OCS (linear) molecules. The masses of the atoms are $m_H = 1$, $m_0 = 16$, $m_C = 12$, $m_S = 32$ in units of the mass of the proton, i.e., 1.67×10^{-24} g. The bond length and bond angle are

$$R_{OH} = 0.96 \text{ Å}$$
$$H_{OH} = 105°$$
$$R_{CO} = 1.16 \text{ Å}$$
$$R_{CS} = 1.56 \text{ Å}$$

8. For $^1H^{35}$ Cl the rotational constant B is 10.6 cm^{-1}. Find the period of a rotation in a rotational level characterised by $l = 4$.
9. Find the degree of degeneracy of the energy levels for a particle in a cubic box with edges of length a and volume a^3 with the following values of $8m, a^2/h^2$; (a) 12, (b) 14, (c) 17.
10. Calculate the first five ($l = 0, 1, 2, 3, 4$) rotational energy levels of a spherical top whose moment of inertia is 4.6×10^{-43} g cm^2 and find the number of spatial orientations the top may adopt in each case.

4

Wave Mechanics of Some Simple Systems where the Potential Energy is not Constant

4.1 One Dimensional Harmonic Oscillator

There are a few simple systems where the potential energy is not constant, yet the Schrödinger equation for such systems can be exactly solved. The simplest examples are given by the vibrations of a diatomic molecule and motions of an atom in a crystal lattice. A model for such systems is a particle of appropriate mass m attracted to a point by a force f proportional to the displacement of the particle as

$$f = -kx \tag{4.1}$$

where k is the force constant for the vibration and x is the displacement from the point of equilibrium. Equation (4.1) is known as Hooke's law. A force of this type is called 'harmonic'. Whenever the motion of a particle can be described by this simple law, the system is referred to as a 'harmonic oscillator'. The potential energy (V) of such a particle equals the integral of this force over the distance it acts:

$$V = -\int_0^x f\,dx = \int_0^x kx\,dx = \tfrac{1}{2}kx^2 \tag{4.2}$$

Classically, the equation of motion is

$$m\frac{d^2x}{dt^2} = -kx \tag{4.3}$$

with the general solution

$$x = a\cos 2\pi\nu_0(t - t_0) \tag{4.4}$$

where a and t_0 are constants and $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$, called the fundamental frequency of the oscillator. The total energy E is given by

$$E = (1/2)m\left(\frac{dx}{dt}\right)^2 + 1/2\,kx^2$$

$$= 2m\pi^2\nu_0^2a^2[\sin^2 2\pi\nu_0(t - t_0) + \cos^2 2\pi\nu_0(t - t_0)] = 1/2\,ka^2 \qquad (4.5)$$

Thus, all positive values of E are allowed. Now we examine the properties of such a system according to the laws of quantum mechanics. The hamiltonian operator for one-dimensional harmonic oscillator is (see Eqs. 2.41 and 4.2)

$$H = -\frac{h^2}{8\pi^2m}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}kx^2 \qquad (4.6)$$

Therefore, the wave equation for this system is,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2m}{h^2}(E - \tfrac{1}{2}kx^2)\psi = 0 \qquad (4.7)$$

and the problem is to find the well-behaved functions which satisfy Eq. (4.7) and the allowed energy levels. Equation (4.7) may be written in the form:

$$\frac{\partial^2\psi}{\partial x^2} + (\alpha - \beta^2x^2)\psi = 0 \qquad (4.8)$$

where

$$\alpha = \frac{8\pi^2m}{h^2}E; \quad \beta = \frac{2\pi}{h}\sqrt{mk} \qquad (4.9)$$

By making the change of variables, $\xi = \sqrt{\beta}\cdot x$ one may rewrite Eq. (4.8) as

$$\frac{\partial^2\psi}{\partial\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0 \qquad (4.10)$$

To solve Eq. (4.10), we shall proceed as follows. Consider a function:

$$y = \exp(-x'^2) \qquad (4.11)$$

Differentiating once, we obtain

$$\frac{\partial y}{\partial x'} + 2x'y = 0 \qquad (4.12)$$

Differentiating $(n + 1)$ more times, we have

$$\frac{\partial^2 Z}{\partial x'^2} + 2x'\frac{\partial Z}{\partial x'} + 2(n + 1)Z = 0 \qquad (4.13)$$

where $$Z = \frac{\partial^n y}{\partial x'^n} = \frac{\partial^n}{\partial x'^n}[\exp(-x'^2)] \qquad (4.14)$$

Assume a function

$$U = (-1)^n \exp\left(\frac{x'^2}{2}\right)\cdot Z \qquad (4.15)$$

Then

$$\frac{\partial^2 U}{\partial x'^2} = \exp\left(\frac{x'^2}{2}\right)\left[\frac{\partial^2 Z}{\partial x'^2} + 2x'\frac{\partial Z}{\partial x'}\right] + Z\cdot\exp\left(\frac{x'^2}{2}\right)(x'^2+1) \qquad (4.16)$$

or
$$\left[\frac{\partial^2 Z}{\partial x'^2} + 2x'\frac{\partial Z}{\partial x'}\right] = \exp\left(-\frac{x'^2}{2}\right)\frac{\partial^2 U}{\partial x'^2} - Z(x'^2+1) \qquad (4.17)$$

Inserting Eq. (4.17) into (4.13) one obtains

$$\frac{\partial^2 U}{\partial x'^2} + [2n+1-x'^2]U = 0 \qquad (4.18)$$

On comparing Eq. (4.18) with Eq. (4.10), we see that the two equations are the same (except for the variables), thus

$$\frac{\alpha}{\beta} = 2n+1 \qquad (4.19)$$

or
$$E = \frac{h}{2\pi}\sqrt{\frac{k}{m}}\cdot(n+\tfrac{1}{2}) \qquad (4.20)$$

Since the classical frequency ν_0 of a vibration is $\frac{1}{2\pi}\sqrt{\frac{k}{m}}$, we write

$$E = (n+\tfrac{1}{2})h\nu_0 \qquad (4.21)$$

where $n = 0, 1, 2, 3, \ldots$ and is called the vibrational quantum number. The state with $n = 0$ is the vibrational ground state which possesses energy $(1/2)h\nu_0$, called the zero-point energy. The occurrence of zero-point energy is consistent with the uncertainty principle.

The solution ψ of Eq. (4.10) is of the form of the function U, given by Eq. (4.15). We have

$$\begin{aligned}\psi &= (-1)^n \exp(\xi^2/2)\frac{\partial^n}{\partial\xi^n}[\exp(-\xi^2)]\\ &= (-1)^n \exp(-\xi^2/2)\exp(\xi^2)\frac{\partial^n}{\partial\xi^n}[\exp(-\xi^2)] \qquad (4.22)\end{aligned}$$

The Hermite polynomial of degree n is defined as

$$H_n(\xi) = (-1)^n \exp(\xi^2)\frac{\partial^n}{\partial\xi^n}[\exp(-\xi^2)] \qquad (4.23)$$

The first few Hermite polynomials are:

$$\left.\begin{array}{ll} H_0(\xi) = 1 & H_2(\xi) = 4\xi^2 - 2 \\ H_1(\xi) = 2\xi & H_3(\xi) = 8\xi^3 - 12\xi \\ H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 & \end{array}\right\} \qquad (4.24)$$

Therefore, the unnormalised wave function of a harmonic oscillator in its n^{th} quantum state of vibration can be written as

$$\psi_n(\xi) = \exp(-\xi^2/2)H_n(\xi) \qquad (4.25)$$

where the first factor $\exp(-\xi^2/2)$ possesses no nodes but it forces ψ to approach zero as ξ tends to $\pm\infty$. On the other hand the function $H_n(\xi)$ introduces n nodes into ψ_n since it is a polynomial with n real roots. Because n can take any integral value or zero, our solution yields the required number of nodes.

The solution of three dimensional oscillator does not create any new problem if the coupling between the oscillations in the directions of the basis vectors, x, y and z is ignored. Such an oscillator is called an isotropic oscillator. The treatment of an anharmonic oscillator in which the driving force does not follow Hooke's law [Eq. (4.1)] cannot be made here because the wave equation in this case does not have the exact solution. It is, therefore, necessary to use the approximation methods for solving the wave equation for the anharmonic oscillator.

4.2 Normalisation and the Characteristics of the Eigenfunctions of a Harmonic Oscillator

The normalisation condition of the wave functions for the oscillator is

$$\int_{-\infty}^{\infty} \psi_n^*(\xi)\psi_n(\xi)\, d\xi = 1 \tag{4.26}$$

Using Eq. (4.25) for ψ_n, it is shown in the Appendix 4 that

$$\int_{-\infty}^{\infty} \exp(-\xi^2)[H_n(\xi)]^2\, d\xi = 2^n \cdot n!\sqrt{\pi} \tag{4.27}$$

The normalised wave functions for the harmonic oscillator are therefore

$$\psi_n(\xi) = \left[\frac{1}{2^n n!\sqrt{\pi}}\right]^{1/2} \exp(-\xi^2/2)H_n(\xi) \tag{4.28}$$

in the range $-\infty < \xi < +\infty$. It can also be shown that for $n \neq n'$, the wave functions are orthogonal, i.e.

$$\int_{-\infty}^{\infty} \psi_n^*(\xi)\psi_{n'}(\xi)\, d\xi = 0 \tag{4.29}$$

The simplest argument for the validity of Eq. (4.29) is that the functions ψ_n and $\psi_{n'}$ are the eigenfunctions of a hamiltonian which is hermitian and possesses different eigenvalues.

The first few energy levels and the corresponding wave functions are shown in Fig. 4.1.

We note that the wave functions characterised by an odd vibrational quantum number are antisymmetrical and those characterised by either zero or an even quantum number are symmetrical about the origin ($\xi = 0$).

4.3 The Recursion formula for the Hermite Polynomials

On introducing Eq. (4.25) into Eq. (4.10), we obtain the following differential equation for the Hermite functions

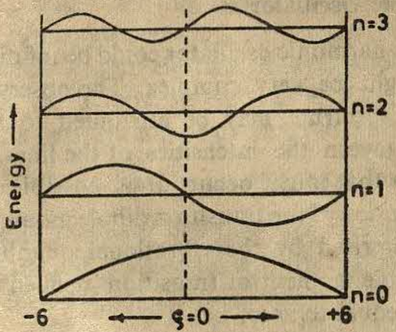

Fig. 4.1 *Energy levels and wave functions of the harmonic oscillator*

$$\frac{\partial^2 H_n}{\partial \xi^2} - 2\xi \frac{\partial H_n}{\partial \xi} + \left(\frac{\alpha}{\beta} - \xi^2\right)H_n(\xi) + (\xi^2 - 1)H_n = 0 \qquad (4.30)$$

Inserting Eq. (4.19) in Eq. (4.30) we get

$$\frac{\partial^2 H_n}{\partial \xi^2} - 2\xi \frac{\partial H_n}{\partial \xi} + 2nH_n = 0 \qquad (4.31)$$

Differentiating twice the Eq. (4.23) one has

$$\frac{\partial^2 H_n}{\partial \xi^2} = 2H_n + 2\xi \frac{\partial H_n}{\partial \xi} - \frac{\partial H_{n+1}}{\partial \xi} \qquad (4.32)$$

Eliminating $\frac{\partial^2 H_n}{\partial \xi^2}$ from Eqs. (4.31) and (4.32) we get

$$2\xi \frac{\partial H_n}{\partial \xi} - 2nH_n = 2H_n + 2\xi \frac{\partial H_n}{\partial \xi} - \frac{\partial H_{n+1}}{\partial \xi} \qquad (4.33)$$

which reduces to

$$\frac{\partial H_{n+1}}{\partial \xi} = 2(n + 1)H_n \qquad (4.34)$$

Since

$$H_{n+1}(\xi) = (-1)^{n+1} \exp(\xi^2/2) \frac{\partial^{n+1}}{\partial \xi^{n+1}} \exp(-\xi^2) \qquad (4.35)$$

$$\frac{\partial H_{n+1}}{\partial \xi} = 2\xi H_{n+1} - H_{n+2} \qquad (4.36)$$

Hence from Eqs. (4.34) and (4.36) we obtain

$$H_{n+2} = 2\xi H_{n+1} - 2(n + 1)H_n \qquad (4.37)$$

This relation will give the higher polynomials. On replacing $(n + 1)$ by n', another integer, we obtain

$$\xi H_{n'} = n'H_{n'-1} + \tfrac{1}{2}H_{n'+1} \qquad (4.38)$$

which is the required recursion formula for the Hermite polynomials.

4.4 The Selection Rules for the Harmonic Oscillator

Since the number of energy levels for a harmonic oscillator could be infinite, it would seem that the spectrum might be very complex. The observed simplicity of the molecular vibration spectrum may be attributed to the operation of 'selection rules' which govern the intensities of the lines or bands associated with many transitions that might occur. It is possible to derive the selection rules by an examination of the transition dipole moment. A transition between two states characterised by the vibrational quantum numbers n and n' is possible if the dipole moment of transition [defined by the left hand side of Eq. (4.39)] is not equal to zero, i.e.

$$e\int_{-\infty}^{\infty} \psi_n^{\bullet} \cdot \hat{X}\psi_{n'}\, dx \neq 0 \tag{4.39}$$

Substituting ψ_n and $\psi_{n'}$ from Eq. (4.28) and using $\xi = \sqrt{\beta} \cdot x$ we may write

$$\begin{aligned} e\int_{-\infty}^{\infty} &\psi_n^{\bullet} \cdot \hat{X}\psi_{n'}\, dx \\ &= \frac{e}{\beta}\left[\frac{1}{2^n n!\sqrt{\pi}}\right]^{1/2} \times \left[\frac{1}{2^{n'} n'!\sqrt{\pi}}\right]^{1/2} \int_{-\infty}^{+\infty} \exp(-\xi^2) H_n \cdot \xi H_{n'}\, d\xi \end{aligned} \tag{4.40}$$

From the recursion formula (4.38),

$$\begin{aligned} \int_{-\infty}^{\infty} &\exp(-\xi^2) H_n \cdot \xi H_{n'}\, d\xi \\ &= \int_{-\infty}^{\infty} \exp(-\xi^2) H_n (n' H_{n'-1} + \tfrac{1}{2} H_{n'+1})\, d\xi \\ &= (N_n N_{n'-1})^{-1} n' \int_{-\infty}^{\infty} \psi_n^{\bullet}\psi_{n'-1}\, d\xi + \tfrac{1}{2}(N_n N_{n'+1})^{-1} \int_{-\infty}^{\infty} \psi_n^{\bullet}\psi_{n'+1}\, d\xi \end{aligned} \tag{4.41}$$

where $N_n N_{n'-1}$ and $N_{n'+1}$ are the normalisation factors for the states ψ_n, $\psi_{n'-1}$ and $\psi_{n'+1}$ respectively. Since wave functions for different states of a harmonic oscillator are mutually orthogonal we can say that the transition dipole moment integral is zero unless $n = n' \pm 1$. The selection rule must be

$$\Delta n = \pm 1 \tag{4.42}$$

for a harmonic oscillator. Therefore, only the fundamental frequency, ν_0 is emitted or absorbed. If the oscillator is somewhat anharmonic, this selection rule is not obeyed and the oscillator can then absorb or emit radiations of frequencies ν_0, $2\nu_0$, $3\nu_0$ . . . and so on. The intensities of the overtone bands give an indication of the amount of anharmonicity of the vibration. (See Sec. 4.14).

4.5 The Hydrogen-like Atoms

We shall now deal with, by the methods of quantum mechanics, the simplest naturally occurring system of chemical interest for which the potential energy is not constant. Such a system which consists of a positively charged nucleus and an electron moving about it is found in the hydrogen atom as well as in ions of He^+, Li^{+2}, Be^{+3}, etc. According to Coulomb's law, the force between a pair of charged particles is operative in the direction of line joining the two charged particles and has the magnitude $F = -\frac{e \cdot Ze}{r^2}$* where $-e$ is the charge of the electron, $+Ze$, the nuclear charge and r, the distance between the two particles. The potential energy resulting from this force is

$$V = -\int_{\infty}^{r} F\,dr = -\frac{Ze^2}{r} \tag{4.43}$$

The Schrödinger equation for the hydrogen-like atom is

$$-\frac{h^2}{8\pi^2 m_e}\nabla^2\psi - \frac{Ze^2}{r}\psi = E\psi \tag{4.44}$$

where m_e is the mass of an electron and it is assumed that the nucleus does not move. As in the case of the rigid rotator this problem is solved by transforming the wave equation into spherical polar coordinates. Such transformation gives rise to the following equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m_e}{h^2}\left(E + \frac{ze^2}{r}\right)\psi = 0 \tag{4.45}$$

Further, it is assumed that the solution has the form

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{4.46}$$

which on substitution into Eq. (4.45) yields the following three equations each containing one variable.

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -m^2 \tag{4.47}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \tag{4.48}$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2 m_e}{h^2}\left(E + \frac{Ze^2}{r}\right)r^2 = \beta \tag{4.49}$$

In these equations, m^2 and β are constants that arise from the separation of variables. The solutions of Eqs. (4.47) and (4.48) are the same as those found for the rigid rotator (Sec. 3.9). The allowed solutions are:

$$\Theta(\theta)\Phi(\phi) = Y_{l\pm m}(\theta, \phi) \tag{4.50}$$

---

*In SI units $F = -\frac{Ze^2}{4\pi\epsilon_0 r^2}$ where ϵ_0 is called permittivity of free space.

where Y is called the spherical harmonic defined by the integers l and m; and $\beta = l(l+1)$ with $l \geqslant |m|$. Substituting for β, $l(l+1)$, one may write Eq. (4.49) as

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{\rho^2 R}{4} + \delta\rho R - l(l+1)R = 0 \tag{4.51}$$

where

$$\alpha^2 = -\frac{8\pi^2 m_e E}{h^2} \tag{4.52}$$

$$\rho = 2\alpha r \tag{4.53}$$

and

$$\delta = \frac{4\pi^2 m_e Z e^2}{h^2\alpha} \tag{4.54}$$

Since

$$\frac{\partial}{\partial r} = 2\alpha\frac{\partial}{\partial \rho} \tag{4.55}$$

Equation (4.51) may be rewritten as

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} - \frac{R}{4} + \frac{\delta R}{\rho} - l(l+1)\frac{R}{\rho^2} = 0 \tag{4.56}$$

For large values of ρ, this reduces to

$$\frac{\partial^2 R}{\partial \rho^2} - \frac{R}{4} = 0 \tag{4.57}$$

and its well-behaved solution is

$$R = \exp\left(-\tfrac{1}{2}\rho\right) \tag{4.58}$$

This seems to suggest that the solution of the Eq. (4.56) for any value of ρ is of the form

$$R = K(\rho)\exp\left(-\tfrac{1}{2}\rho\right) \tag{4.59}$$

where $K(\rho)$ is a function of ρ, whose form is yet to be determined but it should increase less rapidly than $\exp\left(\tfrac{1}{2}\rho\right)$ so that as $\rho \to \infty$, R must vanish. Substituting from Eq. (4.59) in Eq. (4.56) we find

$$\rho^2\frac{\partial^2 K}{\partial \rho^2} + \rho(2-\rho)\frac{\partial K}{\partial \rho} + [(\delta - 1)\rho - l(l+1)]K = 0 \tag{4.60}$$

This equation must be valid for $\rho = 0$, which gives

$$l(l+1)K(0) = 0 \tag{4.61}$$

Thus if $l \neq 0$, $K(0) = 0$

Therefore, if $K(\rho)$ is defined in the form of any power series there should not appear any term in ρ^0. We may then write

$$K(\rho) = \rho^s \sum_{j=0}^{\infty} b_j \rho^j \tag{4.62}$$

where s is a positive number if $l \neq 0$. Substituting from Eq. (4.62) for $K(\rho)$ in Eq. (4.60) we obtain

$$\sum_{j=0}^{\infty}\{[(s+j)(s+j-1) + 2(s+j) - l(l+1)]b_j + (\delta - s - j)b_{j-1}\}\rho^j = 0. \tag{4.63}$$

Since this equation is valid for all values of ρ, the coefficient of each power of ρ vanishes. For the first coefficient, i.e. $j = 0$, we have (there being no coefficient b_{-1} by definition)

$$s(s-1) + 2s - l(l+1) = 0 \tag{4.64}$$

or

$$s(s+1) = l(l+1) \tag{4.65}$$

This means that either $s = l$ or $s = -(l+1)$, but the latter solution is not acceptable due to the restriction given in Eq. (4.61). Therefore, we obtain from Eq. (4.63) the following recursion formula

$$b_{j+1} = \frac{l+j+1-\delta}{(2l+j+2)(j+1)} b_j \tag{4.66}$$

From this relationship we can find the values of all coefficients in the series in terms of the first coefficient, b_0 which may remain as an arbitrary constant. For large values of j, Eq. (4.66) reduces to

$$b_{j+1} \approx bj/j \tag{4.67}$$

This means that $K(\rho)$ behaves roughly in the same way as exp (ρ) and the radial part of the wave function which is related to $K(\rho)$ through Eq. (4.59) is of the form

$$\begin{aligned} R &= \exp(\rho)\cdot\exp(-\tfrac{1}{2}\rho) \\ &= \exp(+\tfrac{1}{2}\rho) \end{aligned} \tag{4.68}$$

for large values of ρ. Obviously this function is not well-behaved and cannot be acceptable. However, the series in Eq. (4.62) may be truncated after some terms (say, for $j = n'$ where n' may be 0, 1, 2, 3, . . .) beyond which all coefficients must vanish. This can happen only if the numerator on the right hand side of Eq. (4.66) vanishes. Thus

$$l + n' + 1 = \delta \tag{4.69}$$

δ is related to the energy through Eqs. (4.54) and (4.52); the energy is therefore quantised since l and n' are integers. If we define a new integer,

$$n = l + n' + 1 \tag{4.70}$$

and make use of Eqs. (4.52) and (4.54), we obtain

$$E = -\frac{2\pi^2 Z^2 e^4 m_e}{n^2 h^2} \tag{4.71}$$

with $n = 1, 2, 3, \ldots$

4.6 The r-dependent Part of the Wave Function

Evidently, according to Eq. (4.71) the energy of the hydrogen atom depends on the quantum number n which is called principal quantum number, but independent of l and m. We see from Eq. (4.70) that l, called angular momentum quantum number, may take up the integral values from 0 to $(n-1)$. Furthermore, for each value of l, there are $2l+1$ possible integral values of m having values from $-l$ to $+l$ through zero. The quantity m is called magnetic quantum number for reasons that will be given later. It must be remembered that the value of n fixes the term at which the series function $K(\rho)$ in Eq. (4.62) breaks off. Making use of Eqs. (4.52), (4.53) and (4.71) we may express ρ as

$$\rho^2 = 4\alpha^2 r^2 = 4\left(\frac{-8\pi^2 m_e E}{h^2}\right) r^2 = \frac{64\pi^4 m_e^2 r^2 z^2 e^4}{n^2 h^4} \tag{4.72}$$

where

$$= \frac{4z^2 r^2}{n^2 a_0^2}$$

$$a_0 = \frac{h^2}{4\pi^2 m_e e^2} = 0.529 \times 10^{-8} \text{ cm} \tag{4.73}$$

The value of a_0 is unity in atomic unit.* We get for the lowest level (i.e., $n = 1$ and $l = 0$) $\rho = 2Zr/a_0$. Then, from the recursion formula (4.66), for $j = 0$, $l = 0$,

$$b_1 = b_0 \frac{l - 1}{2} = 0 \tag{4.74}$$

and therefore $b_2 = b_3 = b_4 = \ldots 0$. The radial part of the wave function for the lowest level is:

$$R_{1,0}(r) = b_0 \exp\left(-\frac{Zr}{a_0}\right) \tag{4.75}$$

For the second level, $n = 2$, l may have the values 0 and 1 and $\rho = Zr/a_0$. The recursion formula (4.66) gives

$$\left.\begin{aligned} &\text{for } j = 0 \;\; l = 0 \;\; b_1 = \frac{1-2}{2} b_0 = -b_0/2 \\ &j = 0 \;\; l = 1 \;\; b_1 = \frac{2-2}{4.1} b_0 = 0 \\ &j = 1 \;\; l = 0 \;\; b_2 = \frac{2-2}{3.2} b_1 = 0 \end{aligned}\right\} \tag{4.76}$$

The radial part of the wave functions for the levels ($n = 2$, $l = 0$ and $n = 2$, $l = 1$) are

$$R_{2,0}(r) = b_0 \left(1 - \frac{Zr}{2a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right) \tag{4.77}$$

$$R_{2,1}(r) = b_0 \left(\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right) \tag{4.78}$$

The radial wave functions are normalised by integrating $R^2(r)$ over the whole of r-space (i.e., from 0 to $+\infty$) and setting the integral equal to unity. From the normalisation procedure, the value of the constant b_0 is determined for the different levels. The normalised radial wave functions for the hydrogen-like atoms are given by

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*In other words, in atomic units $m_e = 1$, $e = 1$ and $h/2\pi = 1$. In SI units $a_0 = (4\pi\epsilon_0)h^2/4\pi^2 m_e e^2$. In atomic units $4\pi\epsilon_0 = 1$.

$$R_{n,l}(r) = -\sqrt{\frac{4(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2Z}{na_0}\right)^3}\left(\frac{2Zr}{na_0}\right)^l \times \exp\left(-\frac{Zr}{na_0}\right) L_{n+1}^{2l+1}\left(\frac{2Zr}{na_0}\right) \tag{4.79}$$

where L_{n+l}^{2l+1} is called the associated Laguerre polynomial of degree $(n-l-1)$. An associated Laguerre polynomial in x of degree $n-m (m \leqslant n)$ is defined as

$$L_n^m(x) = (-1)^n \frac{n!}{(n-m)!}\left[x^{n-m} - \frac{n(n-m)}{1!}x^{nm-1} + \frac{n(n-1)(n-m)(n-m-1)}{2!}x^{n-m-2} + \ldots\right] \tag{4.80}$$

The normalised radial wave functions for the first three values of n are given in Table 4.1.

TABLE 4.1 *Normalised Radial Wave Functions*

n	l	*Wave function*
1	0	$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$
2	0	$R_{2,0} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$
2	1	$R_{2,1} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a^0}\right)^{3/2}\left(\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$
3	0	$R_{3,0} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left[27 - 18\frac{Zr}{a_0} + 2\left(\frac{Zr}{a_0}\right)^2\right] \times \exp\left(-\frac{Zr}{3a_0}\right)$
3	1	$R_{3,1} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left[6\left(\frac{Zr}{a_0}\right) - \left(\frac{Zr}{a_0}\right)^2\right] \times \exp\left(-\frac{Zr}{3a_0}\right)$
3	2	$R_{3,2} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 \exp\left(-\frac{Zr}{3a_0}\right)$

4.7 Total Wave Functions of the Hydrogen-like Atoms

The complete wave functions of the hydrogen-like atoms in spherical polar coordinates are given by

$$\psi(n, l, m) = R_{n,l}(r) Y_{l,\pm m}(\theta, \phi) \tag{4.81}$$

where $Y_{l,\pm m}$ are the normalised spherical harmonics. It is to be noted that the quantum number n determines the energy of the orbital, l, the angular momentum and m, the z-component of the angular momentum. The orbitals with $l = 0, 1, 2, 3$, etc. are respectively called s, p, d, f orbitals. An orbital with $n = 1, l = 0$ is called a $1s$ orbital, with $n = 3, l = 1$ is called $3p$ orbital, etc. It will be noted that there are three p orbitals with $m = 0, +1, -1$. They may be designated as p_0, p_{+1} and p_{-1}. The angular factors associated with these orbitals are, apart from the numerical factors [see Eq. (3.72)].

$$\begin{aligned} p_0 &\sim \cos\theta \\ p_{+1} &\sim \sin\theta \exp(i\phi) \\ p_{-1} &\sim \sin\theta \exp(-i\phi) \end{aligned} \tag{4.82}$$

These functions being complex, have the disadvantage that we cannot draw pictures of them in real space. However, we can obtain functions which are equally good solutions of Eq. (4.45) by taking the following linear combinations of spherical harmonics having the same l values. Thus

$$\frac{1}{\sqrt{2}}(Y_{1,+1} + Y_{1,-1}) = \frac{\sqrt{3}}{2\sqrt{\pi}} \sin\theta\cos\phi \tag{4.83}$$

$$-i/\sqrt{2}(Y_{1,+1} - Y_{1,-1}) = \frac{\sqrt{3}}{2\sqrt{\pi}} \sin\theta\sin\phi$$

Since $\sin\theta\cos\phi$ and $\sin\theta\sin\phi$ are respectively the angular dependence of x and y components of r, the above two combinations are respectively labelled as p_x and p_y atomic orbitals. The total wave functions for different components characterised by $n = 2$, $l = 1$ are shown in Table 4.2.

TABLE 4.2

n	l	m	*Wave function*
2	1	0	$\psi_{2pz} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} r\cos\theta\exp\left(-\frac{Zr}{2a_0}\right)$
2	1	± 1	$\psi_{2px} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} r\sin\theta\sin\phi\exp\left(-\frac{Zr}{2a_0}\right)$ $\psi_{2py} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} r\sin\theta\cos\phi\exp\left(-\frac{Zr}{2a_0}\right)$

4.8 Probability Density in 1s Atomic Orbital

Let us examine the $1s$ orbital of the hydrogen atom ($Z = 1$). According to the wave mechanical theory outlined in this chapter the wave function is given by

$$\psi_{1s} = \left[\frac{1}{\pi a_0^3}\right]^{1/2} \exp\left(-\frac{r}{a_0}\right) \tag{4.84}$$

where r is the distance from the nucleus. The probability density for an electron in this orbital is ψ_{1s}^2 and is given by

$$\psi_{1s}^2 = \frac{1}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right) \tag{4.85}$$

It should be noticed that ψ_{1s}^2 is independent of θ and ϕ and therefore the electron distribution in $1s$ orbital is spherically symmetrical. The plot of ψ_{1s}^2 against r/a_0 is shown in Fig. 4.2. There is another method of describing the electron distribution in an orbital. We determine the probability of an electron being found in a spherical shell of thickness dr at a distance r from the nucleus. It is given by

$$\begin{aligned} P(r)\,dr &= 4\pi r^2 \psi_{1s}^2 dr \\ &= 4\pi r^2 \frac{1}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right) dr \end{aligned} \tag{4.86}$$

We plot $P(r)$ against (r/a_0) in Fig. 4.2. The maximum occurs at a value of r which is found from the equation

$$\frac{\partial P(r)}{\partial r} = \left[-\frac{2r^2}{a_0} + 2r\right] \exp\left(-\frac{2r}{a_0}\right) = 0$$

or

$$r = a_0 \tag{4.87}$$

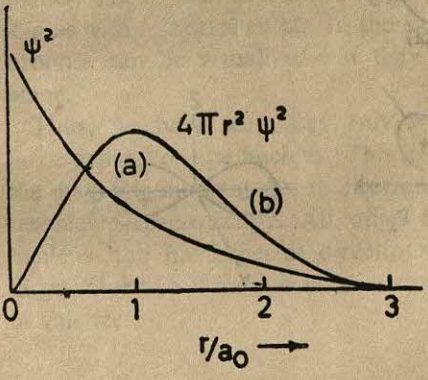

Fig. 4.2 *Probability densities for the 1s hydrogen atomic orbitals*

Thus the maximum radial density occurs at a_o, so that the most probable distance of electron from the nucleus is precisely what has been predicted from the Bohr theory.

It may appear very puzzling to note that, according to the curve (*a*) of Fig. 4.2, the electron density is maximum right on the nucleus while the curve (*b*) shows that electron is most probably found at a distance a_o from the nucleus. This apparent inconsistency may be understood from the following illustration. Consider a number of concentric rings of same thickness but of different radii and made of different materials such that the density of the material decreases as the radius increases. The ring closest to the centre is made of the densest material but does not have the highest mass, because of the smallest volume. On the other hand, a ring of a very large radius may not have the highest mass because of the very small density of its material. But, for a certain intermediate value of the radius the ring should have the largest mass although the density of the material is maximum for the ring closest to the centre.

4.9 Shape of Atomic Orbitals

In the previous section we described the behaviour of 1*s* atomic orbital and the probability functions in terms of *r*. There are other ways in which we can give a pictorial representation of these functions, It is found that the wave functions for 1*s* orbital and for any *s* orbitals for which $l = 0$ are spherically symmetrical. We can draw a spherical boundary surface such that nearly all the electron density (say 99%) is found inside the surface. In a plane, Fig. 4.3(a) may represent the shape of *s*-type atomic orbital. But it is to be noted that the orbitals increase in size as *n* increases.

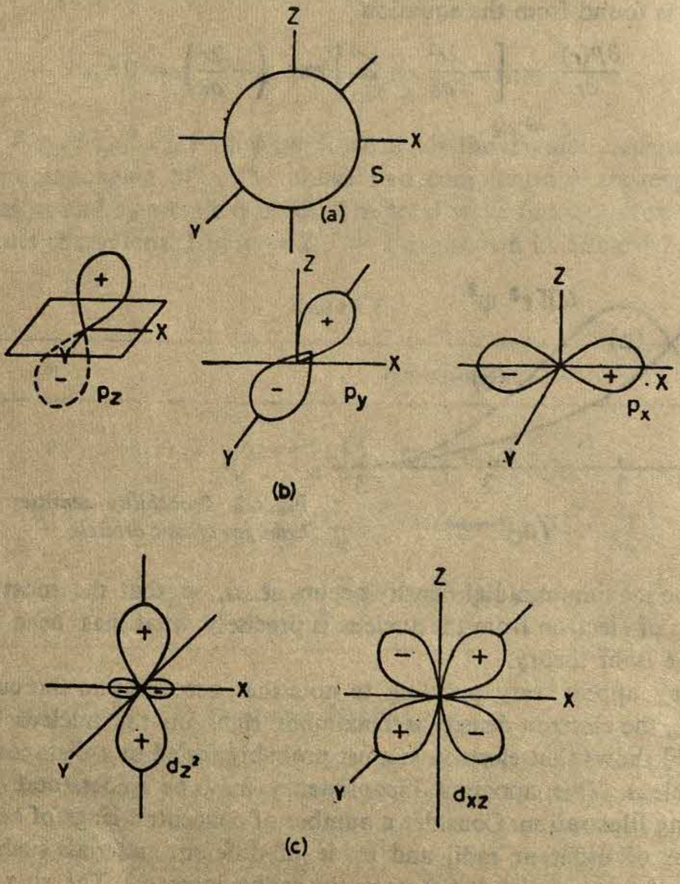

Fig. 4.3 *Shapes of atomic orbitals*

The wave functions for the p type of atomic orbitals (for which $l = 1$) depend on the angular coordinates θ and ϕ in addition to r (see Table 4.2). Further, it is found that the angular functions contain only the quantum numbers l and m whereas the r-functions depend on n and l. The shapes of orbitals are controlled by the angular functions and therefore upon l and m. Let us consider $2p_z$ atomic orbital whose wave function may be written as

$$\psi_{2p_z} = R_{2,1}(r) \cos \theta \tag{4.88}$$

This equation shows that the probability to find an electron at $\theta = \pi/2$, i.e. in the $X - Y$ plane, is zero, in other words the $X - Y$ plane is a nodal plane. The charge is therefore distributed above and below this plane and shows a rotational symmetry around the Z-axis since ψ_{2p_z} is independent of ϕ. This atomic orbital has the shape of a dumbell with positive and negative lobes [Fig. 4.3(b)]. The other two p-orbitals, viz. ψ_{2p_X} and ψ_{2p_Y}, have respectively Y–Z and Z–X as their nodal planes. An important characteristic of these atomic orbitals is that the regions separated by the nodal plane are of opposite signs. However, no physical significance can be attributed to signs of ψ. The physically significant ψ^2 or $\psi^* \cdot \psi$ is always positive.

There are five d orbitals ($l = 2$), two of which are shown in Fig. 4.3(c). In some respects a d orbital is like the superposition of two p-orbitals for there are four similar regions of alternating sign, separated by two nodal planes. The d_z^2 orbital has two large pear-shaped lobes pointing along the Z-axis with a central collar. In the similar way, the f-type and g-type atomic orbitals can be visualised but they are more complicated to draw in a plane.

Thus, we have seen that only s-type of orbitals are spherical and have finite density on the nucleus. This is important in the coupling between the magnetic moment due to electron and that due to nucleus in magnetic resonance spectroscopy. All other types of orbitals have nodes on the nucleus and have special directions in space where the functions have a large value and these special directions play an important role in the theory of valence.

4.10 Physical Interpretations of the Hydrogenic Orbitals

It is possible to prove that the operator $\hat{L}^2$ commutes with the atomic hamiltonian (see Chapter 6). Therefore, the hydrogenic wave functions are the eigenfunctions of the operator for the square of the angular momentum of the electron about an axis passing through the nucleus. If $\hat{L}^2$ has the eigenvalues $l(l + 1)\ (h/2\pi)^2$ (Eq. 3.73), the modulus of the orbital angular momentum vector has the value $[l(l + 1)]^{1/2}\ h/2\pi$ or $\sqrt{l(l + 1)}$ in atomic units where $h/2\pi = 1$.

Suppose that an electron of mass m_e moves about the nucleus in some definite orbit with a velocity v. According to the classical mechanics, the centrifugal force which tends to keep the electron away from the nucleus is given by

$$F = \frac{m_e v^2}{r} = \frac{m_e^2 v^2 r^2}{m_e r^3} = \frac{L^2}{m_e r^3} \tag{4.89}$$

where r is the distance between the electron and the nucleus.

For an electron, using atomic units, $m_e = 1$, and $L^2 = l(l + 1)$, F is given by

$$F = \frac{l(l + 1)}{r^3} \tag{4.90}$$

Thus the radial motion of an electron in an atom is controlled not only by a Coulombic force $-Z/r^2$ but also by a centrifugal force given by Eq. (4.90). The Coulombic force tends to bring electron close to the nucleus whereas the centrifugal force tends to keep the two particles apart. For a stable atom

$$\frac{l(l + 1)}{r^3} - \frac{Z}{r^2} = 0$$

or

$$r = \frac{l(l + 1)}{Z} \tag{4.91}$$

Therefore, we should expect that, other things being equal, an electron in a state of high angular momentum tends to stay farther from the nucleus than an electron in a state of low angular momentum. This is clearly demonstrated in Fig. 4.4 which shows that the higher the value of angular momentum of an electron, the less likely it is to be found close to the nucleus. Thus, for a given value of n, the size of the orbit grows bigger as l increases.

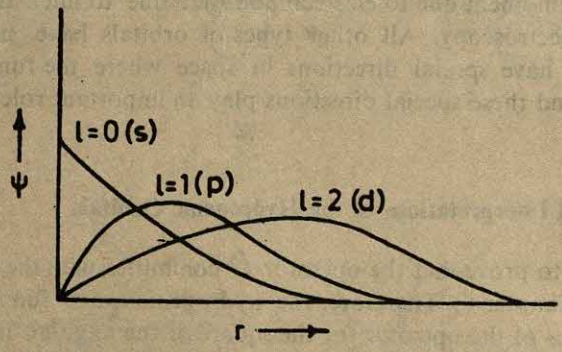

Fig. 4.4 *Shapes of the radial parts of the hydrogenic wave functions of principal quantum number three*

4.11 Space Quantisation of Electronic Orbits

When an electric current flows in a wire bent into the form of a ring, there is generated a magnetic dipole in a direction perpendicular to the plane of the ring. The magnitude of the dipole is given by, according to the law of Biot and Savart,

$$|\mu| = \text{current} \times \text{area of the ring} \tag{4.92}$$

If current is expressed in electrostatic units and the magnetic dipole in electromagnetic units, we have

$$|\mu| = \frac{\pi I a^2}{c} \tag{4.93}$$

where I is the current strength, a the radius of the ring, and c the velocity of light in cm/sec. An electron of charge e moving with a linear velocity v, in a circular orbit of radius a is equivalent to a circular current I, given by

$$I = \frac{ev}{2\pi a} \tag{4.94}$$

Thus

$$|\mu| = \frac{ev}{2\pi a} \times \frac{\pi a^2}{c} = \frac{eva}{2c}$$

$$= \frac{evm_e a}{2m_e c} = \frac{e}{2m_e c} |L|$$

or

$$\mu = \frac{e}{2m_e c} L \tag{4.95}$$

The axis of the magnetic dipole is antiparallel to the angular momentum vector because of the negative charge on the electron (Fig. 4.5). The magnitude of the total angular momentum is given by $\sqrt{l(l+1)}\ h/2\pi$. One may write

$$\mu = \sqrt{l(l+1)} \cdot \beta_e \tag{4.96}$$

where

$$\beta_e = \frac{eh}{4\pi m_e c} \tag{4.97}$$

is the atomic unit of magnetic moment known as Bohr magneton.

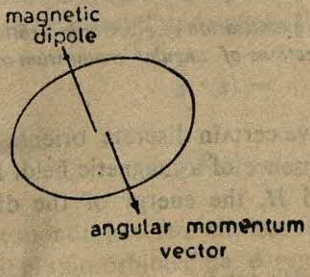

Fig. 4.5 *Relative orientation of the axes of magnetic dipole and rotation*

Since the operator for the component of angular momentum along any chosen direction, say $\hat{L}_z$, has the eigenvalues $mh/2\pi$ (Eq. 3.75) where m can take $2l + 1$ different integral values in the range $-l \leqslant m \leqslant +l$, we may write

$$\cos\theta = \frac{m}{\sqrt{l(l+1)}} \tag{4.98}$$

where θ is the angle between the axis of rotation and the chosen direction Z. This equation clearly demonstrates that $|m|$ cannot exceed $|l|$, otherwise $\cos\theta$ becomes greater than ± 1. This equation also demonstrates that when $m = \pm l$, $\cos\theta$ does not equal ± 1 and therefore, the axis of rotation never coincides with the Z-axis. Figure 4.6 shows the various projections of angular momentum on the Z-axis (for $l = 2$). The component of the magnetic moment in any chosen direction is given by

$$|\mu| \cos\theta = m\beta_0 \tag{4.99}$$

which follows from Eqs. (4.96) and (4.98).

In other words, there are $(2l + 1)$ different components of magnetic moment. Classically, one should expect that the magnetic moment vectors should make all possible angles with any chosen direction. Quantum mechanically, the magnetic moment vectors and hence the electronic orbits can make only certain discrete orientations in space. This is known as the space quantisation of electronic orbits (Fig. 4.6).

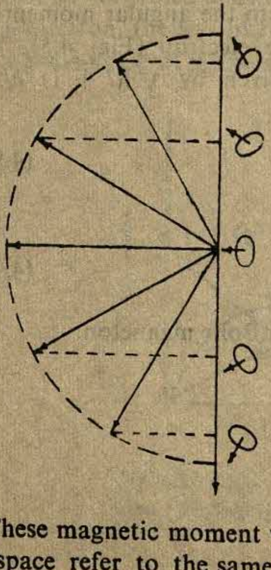

Fig. 4.6 *Space quantisation of electronic orbits and the various projections of angular momentum on the Z-axis*

These magnetic moment vectors which have certain discrete orientations in space refer to the same energy in the absence of a magnetic field. If we place a magnetic dipole μ in a magnetic field H, the energy of the dipole changes by the amount

$$\Delta E = -\mu \cdot H = -|\mu||H|\cos\theta \tag{4.100}$$

where θ is the angle between the dipolar axis and the direction of the magnetic field. Using Eq. (4.99), the interaction energy ΔE may be written as

$$\Delta E = -m\beta_e \mid H \mid \tag{4.101}$$

Thus the magnetic moment vectors which have the different orientations with respect to the external magnetic field have different energies determined by the quantum number m. Because of such association with the magnetic field, the integer m is called the magnetic quantum number. It should be borne in mind that the treatment made here is not a rigorous quantum mechanical one. More rigorous treatment of angular momenta will be found in Chapter 6.

4.12 Electron Spin

A single electron is not completely represented by its wave function $\psi(r)$ which is characterised by three quantum numbers, n, l and m. Even in a state with no orbital angular momentum, application of a magnetic field reveals that the state ψ is really a doublet. The small splitting of the energy levels suggests that the electron possesses an intrinsic magnetic moment. Goudsmit and Uhlenbeck in 1926 postulated that the electron possesses an intrinsic angular momentum, often called spin-angular momentum and a magnetic moment. The component of magnetic moment along the field direction can take only one of two possible values. To describe an electron, in addition to the position variable r, a spin variable s is therefore introduced. The operators associated with the three components of spin angular momentum are denoted by $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ which work on the spin function $\eta(s)$. The complete description of an electron is given by the spin-orbital defined as

$$\phi(r, s) = \psi(r)\eta(s) \tag{4.102}$$

where r is the position variable and $\eta(s)$ is the spin function involving the spin variable. If we are interested in states with a definite value of say, $\hat{S}_z$ then $\eta(s)$ will be a solution of the operator equation:

$$\hat{S}_z\eta(s) = \lambda\cdot\eta(s) \tag{4.103}$$

It is assumed that this equation has only two solutions. They are normally written as α and β and satisfy the following equations.

$$\hat{S}_z\alpha(s) = +\tfrac{1}{2}\frac{h}{2\pi}\cdot\alpha(s)$$

$$\hat{S}_z\beta(s) = -\tfrac{1}{2}\cdot\frac{h}{2\pi}\cdot\beta(s)$$

Corresponding to two choices of spin component, every orbital ψ yields two possible spin orbitals, i.e. $\phi = \psi\alpha$ and $\bar{\phi} = \psi\beta$.

The classical hamiltonian for a particle with magnetic moment μ in a magnetic field H which is along the Z-axis contains the term $H \cdot \mu_z$ [see Eq. (4.100)] in addition to the usual kinetic and potential energy terms. The magnetic moment of the spinning electron along the Z-component is given as [see Eq. (4.96)]

$$\mu_z = -g \frac{e}{2m_e c} \cdot \hat{S}_z \tag{4.104}$$

where g, called the gyro-magnetic ratio for spin, has the value of two. The hamiltonian, $\hat{H}'$ may be written as

$$\hat{H}' = \hat{H}_0 + g \cdot \frac{e}{2m_e c} \mathbf{H} \cdot \hat{S}_z \tag{4.105}$$

where the spin-orbit interaction is neglected. In Eq. (4.105), $\hat{H}_0$ is the sum of kinetic and potential energy operators for the electron. If E_0 be the energy of ψ without the magnetic field, then for $\mathbf{H} \neq 0$, we have

$$\begin{aligned} \hat{H}'\phi(r, s) = \hat{H}'\psi(r)\alpha(s) &= \alpha(s)[\hat{H}_0\psi(r)] + g \frac{e}{2m_e c} \mathbf{H} \cdot \psi(r)[\hat{S}_z\alpha(s)] \\ &= \alpha(s)\,[E_0\psi(r)] + g \frac{e}{2m_e c} \mathbf{H} \cdot \psi(r) \frac{h}{4\pi} \alpha(s) \\ &= [E_0 + \tfrac{1}{2}g\beta_e\mathbf{H}]\,\psi(r)\,\alpha(s) \\ &= [E_0 + \tfrac{1}{2}g\beta_e\mathbf{H}]\,\phi(r, s) \end{aligned} \tag{4.106}$$

where each operator works on its own variables. Thus, in the presence of a magnetic field the energy of ϕ is increased by $\frac{1}{2}g\beta_e\mathbf{H}$. Similarly, the energy of $\bar{\phi}$ is decreased by the same amount (i.e. $-\frac{1}{2}g\beta_e\mathbf{H}$). The corresponding splitting of the doublet is thus $g\beta_e\mathbf{H}$. These two states correspond to different energies and the transition between thesestate ss are accompanied by absorption or emission of radiation whose frequency is given by

$$\Delta E = h\nu \approx g\beta_e\mathbf{H} \tag{4.107}$$

In a field of 3000 gauss, the transition energy corresponds to electromagnetic radiation in the microwave region. The spectra that result from these transitions are called electron spin resonance (ESR) spectra, from which the very accurate value of g is obtained.

Like every eigenfunction, the spin functions must obey the normalisation and orthogonality conditions as follows:

$$\left.\begin{aligned} \int \alpha^*(s)\,\alpha(s)\,ds &= \int \beta^*(s)\,\beta(s)\,ds = 1 \\ \int \alpha^*(s)\,\beta(s)\,ds &= \int \beta^*(s)\,\alpha(s)\,ds = 0 \end{aligned}\right\} \tag{4.108}$$

where the integration is over the spin space.

4.13 Energy of the Hydrogen Atom and the Isoelectronic Ions

The minimum energy which is required to remove an electron from the hydrogen atom in its ground state is the first ionisation potential. It is equal to the negative of the first eigenvalue which according to Eq. (4.71) is

$$E_1 = -\frac{2\pi^2 m_e e^4}{h^2} = -13.6 \text{ eV} \tag{4.109}$$

In the system of atomic units, the radius of the first Bohr orbit of the hydrogen atom given by Eq. (4.73) is said to have unit length and $e^2 = 1$, therefore Eq. (4.109) may be written as

$$E_1 = -\tfrac{1}{2} \tag{4.110}$$

and the wave equation for the hydrogen atom takes the following simple form

$$-\tfrac{1}{2}\nabla^2\psi - \frac{1}{r}\psi = E\psi \tag{4.111}$$

The energy levels of the hydrogen atom in atomic units may be expressed as

$$E_n = -\frac{1}{2n^2} \tag{4.112}$$

Atoms that are isoelectronic with hydrogen atom, are, for example, He^+, Li^{++}, Be^{+++}, etc., in which electron is subjected to the potential Z/r where Z is 2, 3, 4, etc. respectively. The wave equation for these systems is of the form:

$$-\tfrac{1}{2}\nabla^2\psi - \frac{Z}{r}\psi = E\psi \tag{4.113}$$

where the first eigenvalue or the lowest energy is given as

$$E_1 = -Z^2/2 \tag{4.114}$$

and the wavefunction of the 1*s* atomic orbital, for example, is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} Z^{3/2} \exp(-Zr) \tag{4.115}$$

The most probable distance between the electron and the nucleus may be found by following a similar procedure described in Section 4.8 for the hydrogen atom and is given by

$$\hat{r} = \frac{1}{Z} \tag{4.116}$$

This shows that as the atomic number increases the orbital contracts. Also, the first ionisation potential increases as Z increases. The observed first ionisation potentials of He^+, Li^{++} and Be^{+++} ions, are:

He^+ : 54.16 eV
Li^{++} : 121.8 eV
Be^{+++} : 216.6 eV

4.14 Vibration and Vibrational Spectra of Diatomics

When one deals with vibrations of a diatomic molecule, one sees only a single mode of oscillation, i.e., the stretching and contracting of bond. This stretching and contracting of the bond can be treated to a good approximation as simple harmonic oscillation about the equilibrium bond length. Therefore, the permitted vibrational energy levels are given by Eq. (4.21) with

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$$

Here, we come across a difficulty about the mass m. This mass m is not the total mass of the molecule. For example, if one of the atoms is extremely heavy relative to the other atom one may imagine that the smaller mass is attached by a weightless spring to a massive body which is fixed and the fundamental frequency ν_0 may be determined by the smaller mass.

Consider two atoms of masses m_1 and m_2 separated by the bond length R. The centre of mass is determined by

$$m_1r_1 = m_2r_2$$

where $r_1 + r_2 = R$. We have

$$r_1 = \frac{m_2}{m_1 + m_2}R \qquad \text{and} \qquad r_2 = \frac{m_1}{m_1 + m_2}R$$

Therefore, the equations of motion for each atom are given as

$$m_1\frac{d^2r_1}{dt^2} = -K(R - R_e), \qquad m_2\frac{d^2r_2}{dt^2} = -K(R - R_e)$$

where R_e is the equilibrium bond length.

Substitutions for r_1 and r_2 in the two equations give

$$\mu\frac{d^2R}{dt^2} = -K(R - R_e) \tag{4.117}$$

$$\mu = \frac{m_1m_2}{m_1 + m_2} \tag{4.118}$$

where μ is called the reduced mass of the molecule. One can now imagine that a particle of mass μ is undergoing simple harmonic motion along R with the frequency

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

If the vibration is harmonic then the energy levels will be given by Eq. (4.21) and the selection rule for transition should be given by Eq. (4.42). Thus, one expects a single line with frequency ν_0 in the vibrational spectra of diatomic molecules.

But, in reality, one observes many lines with weaker intensities than that of the fundamental line in the pure vibration spectrum. One reason for this is that the nuclear vibrations deviate from that of the harmonic oscillator. A schematic diagram of the actual potential energy vs. internuclear distance, R, in a diatomic molecule is shown in Fig. 4.7 where the dashed lines indicate the parabolic potential curve used for harmonic oscillator.

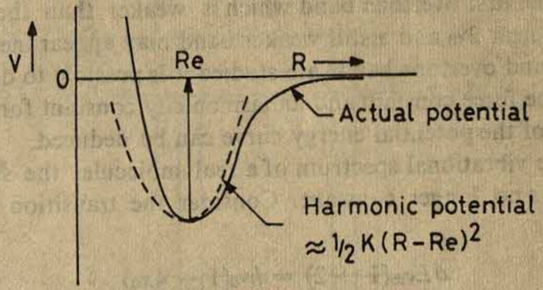

Fig. 4.7 *The real potential energy curve (solid line) and the parabolic potential energy curve (dashed line) vs. R*

The shape of the actual potential energy curve as shown in Fig. 4.7 arises from the fact that every diatomic molecule dissociates into atoms at large displacement from the equilibrium positions of the nuclei. The most commonly used approximation of the potential energy of a diatomic molecule is the Morse function given by

$$V(R) = D_e\{1 - \exp[-a(R - R_e)]\}^2 \tag{4.119}$$

For large R, the potential energy approaches D_e where D_e is the dissociation energy and a is a constant. In fact, the Schrödinger equation can be solved with $V(R)$ given by Eq. (4.119). The energy eigenvalues of the Morse potential are given by[1]

$$E_{\text{vib}} = h\nu_0[(n + \tfrac{1}{2}) - x_0(n + \tfrac{1}{2})^2] \tag{4.120}$$

where x_0 may be called the anharmonicity constant and is given by $h\nu_0/4D_e$. The energy of the fundamental transition 0 → 1 is now given by

$$E_{\text{vib}}(0 \rightarrow 1) = h\nu_0(1 - 2x_0) \tag{4.121}$$

Molecular vibrations are studied by observing the vibrational absorption spectra which for diatomic molecules are found primarily in the infra-red region corresponding to wavenumbers 200 ~ 4000 cm^{-1}.

In Sec. 4.4 we have derived that the transition dipole moment or instantaneous dipole moment is different from zero if $\Delta n = \pm 1$. It is, therefore, immediately clear that a homonuclear diatomic molecule whose dipole moment is always zero for all values of the nuclear displacement cannot give rise to pure vibrational spectrum. Besides, the vibrations in real diatomic molecules are not strictly harmonic, so they can exhibit transitions with

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[1] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co. (1935).

$\Delta n = \pm 2$, ± 3, etc. But these are less probable than those with $\Delta n = \pm 1$. Let us now consider the transition $0 \rightarrow 2$. From Eq. (4.120) the energy of the first overtone band is given by

$$\Delta E_{\text{vib}}(0 \rightarrow 2) = 2h\nu_0(1 - 3x_0) \tag{4.122}$$

We see that the first overtone band which is weaker than the fundamental band appears near $2\nu_0$ and a still weaker band may appear near $3\nu_0$. If the fundamental and overtone bands are studied it is possible to derive informations about the force constant and anharmonicity constant for the bond, and so the shape of the potential energy curve can be deduced.

Also, in the vibrational spectrum of a real molecule, the spacing of the energy levels is no longer constant. Consider the transition $1 \rightarrow 2$, ΔE is given by

$$\Delta E_{\text{vib}}(1 \rightarrow 2) = h\nu_0(1 - 4x_0) \tag{4.123}$$

If we compare Eq. (4.123) with Eq. (4.121) we find that the transition $0 \rightarrow 1$ requires more energy than the transition $1 \rightarrow 2$ and so on. The vibration spectrum therefore consists of many lines rather than one as predicted for a simple harmonic oscillator (see Sec. 4.4).

Since a real molecule may vibrate and rotate simultaneously, it can undergo transitions in which both the quantum numbers l and n change. The rotational constant may depend on the vibrational state because the vibrations may affect the moment of inertia. So the rotational constant B should be labelled with the vibrational quantum number n. The energy of a rotating-vibrating diatomic molecule is given by

$$\begin{aligned} E(n, l) = h\nu_0[(n + 1/2) - x_0(n + 1/2)^2] \\ + B_n\, l(l + 1) \end{aligned} \tag{4.124}$$

where the anharmonicity effect is included. For the ground electronic states, the selection rules are those we have already introduced, i.e.,

$$\Delta n = \pm 1, \qquad \Delta l = \pm 1$$

when $\Delta l = +1$, the transition energies in the vibrational spectrum, characterised by $n \rightarrow n + 1$, are given by

$$\Delta E = \Delta E_{\text{vib}}^{(n \rightarrow n+1)} + 2B_n(l + 1) \tag{4.125}$$

where we assume that the rotational constants are the same in the upper and lower vibrational states and $\Delta E_{\text{vib}}(n \rightarrow n + 1)$ is the vibrational part of the energy difference. According to Eq. (4.125) one expects a series of lines separated by $2B_n$. These lines constitute the R-branch of the spectrum (see Fig. 4.8). When $\Delta l = -1$, the corresponding transition energies are given by

$$\Delta E = \Delta E_{\text{vib}}(n \rightarrow n + 1) - 2B_n l \tag{4.126}$$

These lines appear on the low energy side of the fundamental vibration band. They are called the P-branch (see Fig. 4.8). When the rotational constants B are not the same in the initial and final vibrational states, the spacing between the lines in either branch is no longer regular.

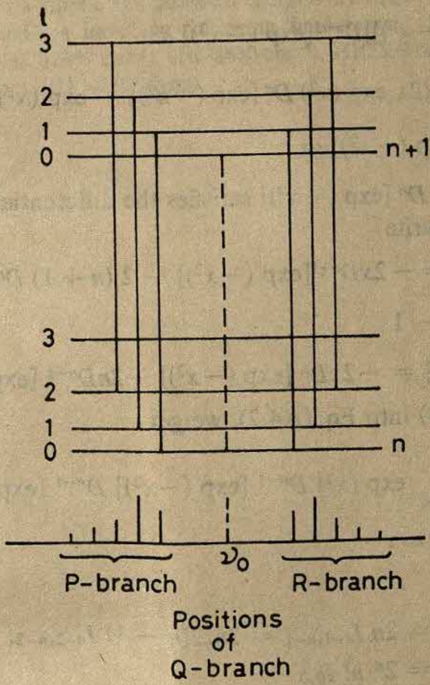

Fig. 4.8 *Position of P, Q and R branches in vibration-rotation spectra*

A Q-branch results from a transition in which $\Delta l = 0$. It appears in the vibrational spectra of those molecules for which the angular momentum parallel to the internuclear axis is not zero.

APPENDIX 4

We shall evaluate the following integral

$$I_{n,n} = \int_{-\infty}^{\infty} \exp(-x^2) H_n(x) H_n(x)\, dx \tag{A4.1}$$

where $Hn(x)$ is the Hermite polynomial of variable x and of the degree n, and is defined by Eq. (4.23) in the text. Writing D, for the differential d/dx, one can write the integral $I_{n,n}$ as

$$I_{n,n} = \int_{-\infty}^{\infty} \exp(x^2)\,(-1)^{2n} D^n [\exp(-x^2)]\, D^n[\exp(-x^2)]\, dx$$

$$= \Big[\exp(x^2)\, D^n [\exp(-x^2)]\, D^{n-1} [\exp(-x^2)]\Big]_{-\infty}^{\infty}$$

$$- \int_{-\infty}^{\infty} \{2x \exp(x^2)\, D^n [\exp(-x^2)] + \exp(x^2)\, D^{n+1} [\exp(-x^2)]\} D^{n-1}[\exp(-x^2)]\, dx$$

$$= 0 - \int_{-\infty}^{\infty} \{2x \exp(x^2)\, D^n [\exp(-x^2)] + \exp(x^2)\, D^{n+1} [\exp(-x^2)]\} \times D^{n-1} [\exp(-x^2)]\, dx \qquad \text{(A4.2)}$$

Since the function $D^n [\exp(-x^2)]$ satisfies the differential equation (4.13) of the text one may write

$$D^{n+2}[\exp(-x^2)] = -2xD^{n+1}[\exp(-x^2)] - 2(n+1)\, D^n[\exp(-x^2)] \qquad \text{(A4.3)}$$

Replacing n by $n - 1$

$$D^{n+1} [\exp(-x^2)] = -2xD^n [\exp(-x^2)] - 2nD^{n-1} [\exp(-x^2)] \qquad \text{(A4.4)}$$

Inserting Eq. (A4.4) into Eq. (A4.2), we get

$$I_{n,n} = 2n \int_{-\infty}^{\infty} \exp(x^2)\, D^{n-1} [\exp(-x^2)]\, D^{n-1} [\exp(-x^2)]\, dx \qquad \text{(A4.5)}$$

$$= 2n\, I_{n-1,n-1}$$

Thus

$$I_{n,n} = 2n\, I_{n-1,n-1} = 2n.\, 2(n-1)\, I_{n-2,n-2} \cdots$$

$$= 2^n \cdot n!\, I_{0,0} \qquad \text{(A4.6)}$$

Since

$$I_{0,0} = \int_{-\infty}^{\infty} \exp(-x^2)\, dx = \sqrt{\pi} \qquad \text{(A4.7)}$$

We find that

$$I_{n,n} = 2^n \cdot n! \sqrt{\pi} \qquad \text{(A4.8)}$$

PROBLEMS

1. Calculate the zero-point energy of a mass of 1.67×10^{-24} gm connected to a fixed point by a spring with a force constant of 10^4 dyne/cm.
2. Calculate the mean value of the potential energy experienced by an electron in the 1*s*-orbital of the hydrogen atom. Show that the average kinetic energy is equal to the total energy with the sign changed.
3. Consider two non-orthogonal orbitals, $\phi_1 = N_1 e^{-r}$ and $\phi_2 = N_2 r e^{-r}$, where N_1 and N_2 are the normalising factors. Find N_1 and N_2 and construct a pair of orthogonal functions from ϕ_1 and ϕ_2.
4. Show that electron density in a filled shell of orbitals, like the configurations p^6 and d^{10}, is spherically symmetrical.

5. In the vibrational spectrum of HCl the first three energy levels appear at 1331.8 cm^{-1}, 3917.4 cm^{-1} and 6398.94 cm^{-1}. Find the corresponding harmonic oscillator wavenumber ω_0, its anharmonicity constant, x_0, and dissociation energy D_e.
6. For the ground state of the one-dimensional harmonic oscillator show that the average value of its kinetic and potential energies are equal.
7. The hydrogen halides have the following fundamental vibration frequencies: HF(4141 cm^{-1}), HCl(2989 cm^{-1}), HBr(2650 cm^{-1}), HI(2309 cm^{-1}). Find their force constants in N/cm. (lN = 10^5 dyne).

5

Approximation Methods and Interaction of Radiation and Matter

5.1 Introduction

The systems considered in the preceding chapters are those for which Schrödinger's equation can be solved exactly and therefore their true wave functions, energies and other properties are obtained. However, for most problems of chemical interest the Schrodinger equation cannot be solved exactly because in these problems the presence of more than one electron introduces the electron repulsion terms (i.e. e^2/r_{ij} where r_{ij} is the distance between electron i and electron j) in the hamiltonian. The separation of variables as was possible in the treatment of the hydrogen atom cannot be possible now owing to the dependence of r_{ij} on θ and ϕ coordinates. Therefore, for systems having more than one electron it is not feasible to obtain an exact solution of the wave equation which has to be solved approximately. The Schrödinger equation cannot also be solved exactly for one-electron system whose potential field is not spherically symmetrical (e.g. hydrogen atom in an electric or magnetic field). There are two commonly used methods for obtaining approximate solutions to the wave equation. They are: (1) the perturbation method; and (2) the variation method. The perturbation method is generally suitable for a system which differs in a very small way from one for which the exact solution is known. In fact, this method is successfully applied to obtain the wave functions and energies of the hydrogen atom in presence of a weak electric field. The variation method is applicable to those systems for which the wave functions can be guessed. The trial wave function ought to be close to the true wave function of the system concerned and the mean energy is then calculated. This is taken to be the energy of the system. Unfortunately, in many cases, it is difficult to guess what the true wave function will be like.

In this and the following chapters we shall always use for convenience the bracket notation for the integral over all variables: Thus

$$\langle f \mid A \mid g \rangle = \int f \cdot \hat{A} g \, d\tau$$

where f and g are functions, $\hat{A}$, an operator, $d\tau$, the collective symbol for the volume element over all variables. The function f appearing at the left, inside the bracket, refers to its complex conjugate if f is not a real function.

5.2 General Time-independent Perturbation Theory

The kinds of problems which can be successfully dealt with by the perturbation theory are those for which the following conditions are satisfied. They are:

(1) The hamiltonian can be decomposed into two parts as

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}$$

where $\lambda \hat{V}$ is the perturbation, and λ is the expansion parameter.

(2) The eigenvalues and eigenfunctions of the unperturbed hamiltonian $\hat{H}^{(0)}$ are known.

(3) $\hat{H}^{(0)} \gg \lambda \hat{V}$

Let $\psi^{(0)}$ be the wave function of $H^{(0)}$ with $E^{(0)}$ as its eigenvalue. Then the unperturbed eigenvalue equation is

$$\hat{H}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)} \tag{5.1}$$

Let ψ be the wave function of the hamiltonian $\hat{H}$, then the eigenvalue equation which we wish to solve is

$$(\hat{H}^{(0)} + \lambda(\hat{V})\, \psi = E\psi \tag{5.2}$$

If λ is set equal to zero, Eq. (5.2) reduces to Eq. (5.1), so that E becomes $E^{(0)}$ and ψ becomes $\psi^{(0)}$. The effect of perturbation $\lambda \hat{V}$ is to change slightly the unperturbed eigenvalue $E^{(0)}$ to E and the unperturbed eigenfunction $\psi^{(0)}$ to ψ. Since ψ and E are functions of λ, we expand them in the form of a power series as

$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \lambda^3 \psi^{(3)} + \ldots \tag{5.3}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots \tag{5.4}$$

where $\psi^{(1)}, \psi^{(2)}, \ldots$ and $E^{(1)}, E^{(2)} \ldots$ are independent of λ and $\psi^{(1)}, \psi^{(2)} \ldots$ are so chosen that they are orthogonal to $\psi^{(0)}$ which is assumed to be normalised. If we substitute these series in Eq. (5.2) we find the following equation for the perturbed system.

$$\hat{H}^{(0)}(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots) + \lambda\hat{V}(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots)$$
$$= (E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots)(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots) \tag{5.5}$$

Before finding the solution of this equation one has to decide to what order of accuracy the eigenfunctions and eigenvalues of the perturbed system are required. Since the perturbed system is only slightly different from the unperturbed one, one may treat $\psi^{(0)}$ and $E^{(0)}$ as being the approximate solutions of the perturbed system. This is called the zeroth order approximation to the true solution of the perturbed system. If one wishes to obtain more accurate eigenfunctions and eigenvalues of Eq. (5.5) one has to retain the larger number of terms in the series (5.3) and (5.4) and then solve Eq. (5.5). Thus, in the first-order perturbation theory, we approximate the true solution to the eigenvalue equation by retaining the second terms in the series (5.3) and (5.4). Similarly, in the second-order perturbation theory, we retain the third terms involving λ^2 in the series (5.3) and (5.4) and so on. Therefore, equating the coefficients of the various powers of λ in Eq. (5.5) as λ is an arbitrarily small parameter, one obtains the series of equations

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \tag{5.6}$$

$$(\hat{H}^{(0)} - E^{(0)})\psi^{(1)} = -\hat{V}\psi^{(0)} + E^{(1)}\psi^{(0)} \tag{5.7}$$

$$(\hat{H}^{(0)} - E^{(0)})\psi^{(2)} = -\hat{V}\psi^{(1)} + E^{(2)}\psi^{(0)} + E^{(1)}\psi^{(1)} \tag{5.8}$$

$$(\hat{H}^{(0)} - E^{(0)})\psi^{(3)} = -\hat{V}\psi^{(2)} + E^{(3)}\psi^{(0)} + E^{(2)}\psi^{(1)} + E^{(1)}\psi^{(2)} \tag{5.9}$$

$$\begin{aligned}(\hat{H}^{(0)} - E^{(0)})\psi^{(4)} = -\hat{V}\psi^{(3)} + E^{(4)}\psi^{(0)} + E^{(3)}\psi^{(1)} + E^{(2)}\psi^{(2)} \\ + E^{(0)}\psi^{(3)}\end{aligned} \tag{5.10}$$

The first of these equations, i.e. Eq. (5.6) is already solved. If the second one can be solved we obtain $\psi^{(1)}$ and $E^{(1)}$. The solution of the third one gives $\psi^{(2)}$ and $E^{(2)}$, and so on.

To obtain the first-order perturbation energy we multiply Eq. (5.7) with $\psi^{(0)*}$ on both sides and integrate over the whole space. Thus, using the bracket notation for the integral, we have

$$\langle \psi^{(0)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(1)} \rangle = -\langle \psi^{(0)} \mid V \mid \psi^{(0)} \rangle + E^{(1)} \langle \psi^{(0)} \mid \psi^{(0)} \rangle \tag{5.11}$$

Since $\hat{H}^{(0)}$ is hermitian one may write the integral on the left hand side of Eq. (5.11) as

$$\langle \psi^{(0)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(1)} \rangle = \langle \psi^{(1)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(0)} \rangle^{*}$$

We assume here and in subsequent sections that all wave functions are real. From Eq. (5.6), it follows

$$\langle \psi^{(1)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(0)} \rangle = 0 \tag{5.12}$$

Therefore

$$E^{(1)} = \langle \psi^{(0)} \mid V \mid \psi^{(0)} \rangle \tag{5.13}$$

since $\psi^{(0)}$ is chosen normalised.

To obtain second-order perturbation energy we similarly multiply Eq. (5.8) with $\psi^{(0)}$ on both sides and integrate over the whole space.

$$\begin{aligned} \langle \psi^{(0)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(2)} \rangle &= -\langle \psi^{(0)} \mid V \mid \psi^{(1)} \rangle \\ &+E^{(2)} \langle \psi^{(0)} \mid \psi^{(0)} \rangle + E^{(1)} \langle \psi^{(0)} \mid \psi^{(1)} \rangle \end{aligned} \tag{5.14}$$

Using the hermitian property of $\hat{H}^{(0)}$, and remembering that $\psi^{(1)}$ is chosen orthogonal to $\psi^{(0)}$ which is assumed normalised, one obtains

$$E^{(2)} = \langle \psi^{(0)} \mid V \mid \psi^{(1)} \rangle \tag{5.15}$$

Similarly one can deduce that

$$E^{(3)} = \langle \psi^{(0)} \mid V \mid \psi^{(2)} \rangle \tag{5.16}$$

$$E^{(4)} = \langle \psi^{(0)} \mid V \mid \psi^{(3)} \rangle \tag{5.17}$$

and

$$E^{(n)} = \langle \psi^{(0)} \mid V \mid \psi^{(n-1)} \rangle \tag{5.18}$$

These equations show that the calculation of the n^{th} order energy requires the knowledge of $(n - 1)$th order eigenfunctions. However, the perturbation theory is in reality more powerful than the above results seem to indicate. One can show that a knowledge of the wave function to an order of n suffices to determine the eigenvalue to the order $2n + 1$.[1]

For example, $E^{(4)}$ in Eq. (5.17) can be obtained without knowing $\psi^{(3)}$. For

$$\begin{aligned} E^{(4)} &= \langle \psi^{(0)} \mid V \mid \psi^{(3)} \rangle = \langle \psi^{(3)} \mid V \mid \psi^{(0)} \rangle \\ &= -\langle \psi^{(3)} \mid (H^{(0)} - E^{(0)})\psi^{(1)} \rangle + E^{(1)} \langle \psi^{(3)} \mid \psi^{(0)} \rangle \\ &= -\langle \psi^{(3)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(1)} \rangle \\ &= -\langle \psi^{(1)} \mid (H^{(0)} - E^{(0)}) \mid \psi^{(3)} \rangle \\ &= \langle \psi^{(1)} \mid V \mid \psi^{(2)} \rangle - E^{(3)} \langle \psi^{(1)} \mid \psi^{(0)} \rangle - E^{(2)} \langle \psi^{(1)} \mid \psi^{(1)} \rangle \\ &\quad - E^{(1)} \langle \psi^{(1)} \mid \psi^{(2)} \rangle \qquad \text{(See Eq. 5.9)} \\ &= \langle \psi^{(1)} \mid V \mid \psi^{(2)} \rangle - E^{(2)} \langle \psi^{(1)} \mid \psi^{(1)} \rangle - E^{(1)} \langle \psi^{(1)} \mid \psi^{(2)} \rangle \end{aligned} \tag{5.19}$$

Thus to calculate $E^{(4)}$ the knowledge of $\psi^{(3)}$ is not needed. One can similarly find a corresponding formula for $E^{(5)}$ which depends on $\psi^{(0)}$, $\psi^{(1)}$ and $\psi^{(2)}$. Thus, $E^{(1)}$, $E^{(2)}$ and $E^{(3)}$ can be derived from $\psi^{(1)}$, $E^{(4)}$ and $E^{(5)}$ from $\psi^{(2)}$, and, so on.

So far we have not made any attempt to solve Eqs. (5.7), (5.8), (5.9), etc. Let us consider Eq. (5.7). To solve this it is customary to expand $\psi^{(1)}$ in terms of the complete set of eigenfunctions of the unperturbed hamiltonian $H^{(0)}$. Let us specify an eigenvalue with a subscript i. Then the unperturbed equation is

$$\hat{H}^{(0)}\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)} \tag{5.20}$$

With $i = 1, 2, 3, 4, \ldots$

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[1] A. Dalgarno and A.L. Stewart, *Proc. R. Soc.*, 238A, 275, 1956.

where $E_i^{(0)}$ is non-degenerate, i.e. there is only one normalised eigenfunction belonging to each $E_i^{(0)}$. Then

$$\psi_i^{(1)} = \sum_{j \neq i} C_{ij} \psi_j^{(0)} \tag{5.21}$$

The summation in Eq. (5.21) includes, if necessary, an integration over the continuous eigenspectrum of $\hat{H}^{(0)}$. The omission from the sum of the state $i = j$ ensures that $\psi_i^{(1)}$ is orthogonal to $\psi_i^{(0)}$. Thus, the integral is written as

$$\langle \psi_i^{(0)} \mid \psi_i^{(1)} \rangle = \sum_{j \neq i} C_{ij} \langle \psi_i^{(0)} \mid \psi_j^{(0)} \rangle = 0$$

because the set of eigenfunctions ψ_i^0, ψ_j^0 etc. of $H^{(0)}$ is orthonormal.

Substituting from Eq. (5.21) in an equation of the form (5.7) for $\psi_i^{(1)}$ one obtains

$$(\hat{H}^{(0)} - E_i^{(0)}) \sum_{j \neq i} C_{ij} \psi_j^{(0)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

or

$$\sum_{j \neq i} C_{ij}(E_j^{(0)} - E_i^{(0)})\psi_j^{(0)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)} \tag{5.22}$$

If we multiply Eq. (5.22) with $\psi_i^{(0)}$ and integrate overall space, we have

$$\sum_{j \neq i} C_{ij}(E_j^{(0)} - E_i^{(0)}) \langle \psi_i^{(0)} \mid \psi_j^{(0)} \rangle$$
$$= -\langle \psi_i^{(0)} \mid V \mid \psi_i^{(0)} \rangle + E_i^{(1)} \langle \psi_i^{(0)} \mid \psi_i^{(0)} \rangle \tag{5.23}$$

The left hand side of Eq. (5.23) is zero. Thus

$$E_i^{(1)} = \langle \psi_i^{(0)} \mid V \mid \psi_i^{(0)} \rangle \tag{5.24}$$

We shall now seek the first-order correction to the wave function. Let us expand the summation in Eq. (5.22)

$$C_{i1}(E_1^{(0)} - E_i^{(0)})\psi_1^{(0)} + C_{i2}(E_2^{(0)} - E_i^{(0)})\psi_2^{(0)} + C_{i3}(E_3^{(0)} - E_i^{(0)})$$
$$\times \psi_3^{(0)} + \ldots = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)} \tag{5.25}$$

In order to obtain C_{i1} we multiply both sides of this equation with $\psi_1^{(0)}$ and integrate over the whole space:

$$C_{i1}(E_1^{(0)} - E_i^{(0)}) \langle \psi_1^{(0)} \mid \psi_1^{(0)} \rangle + C_{i2}(E_2^{(0)} - E_i^{(0)}) \langle \psi_1^{(0)} \mid \psi_2^{(0)} \rangle$$
$$+ C_{i3}(E_3^{(0)} - E_0^{(0)}) \langle \psi_1^{(0)} \mid \psi_3^{(0)} \rangle + \ldots$$
$$= -\langle \psi_1^{(0)} \mid V \mid \psi_i^{(0)} \rangle + E_i^{(1)} \langle \psi_1^{(0)} \mid \psi_i^{(0)} \rangle$$

Since the zero-order wave functions are orthogonal and normalised we have

$$C_{i1} = -\frac{\langle \psi_1^{(0)} \mid V \mid \psi_i^{(0)} \rangle}{E_1^{(0)} - E_i^{(0)}}$$

Similarly, to obtain C_{i2} we multiply both sides of Eq. (5.25) with $\psi_2^{(0)}$ and integrate. We have then

$$C_{i2} = -\frac{\langle \psi_2^{(0)} \mid V \mid \psi_i^{(0)} \rangle}{E_2^{(0)} - E_i^{(0)}}$$

Thus, one can write

$$C_{ij} = -\frac{\langle \psi_j^{(0)} \mid V \mid \psi_i^{(0)} \rangle}{E_j^{(0)} - E_i^{(0)}} \tag{5.26}$$

Substituting for C_{ij} from Eq. (5.26) in Eq. (5.21) one obtains the first-order correction to the wave function:

$$\begin{aligned} \psi_i^{(1)} &= -\sum_{j\neq i} \frac{\langle \psi_j^{(0)} \mid V \mid \psi_i^{(0)} \rangle}{E_j^{(0)} - E_i^{(0)}} \psi_j^{(0)} \\ &= \sum_{j\neq i} \frac{\langle \psi_j^{(0)} \mid V \mid \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} \psi_j^{(0)} \end{aligned} \tag{5.27}$$

We can now summarise the results of the non-degenerate first-order perturbation theory as:

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} = E_i^{(0)} + \lambda \langle \psi_i^{(0)} \mid V \mid \psi_i^{(0)} \rangle \tag{5.28a}$$

$$\begin{aligned} \psi_i &= \psi_i^{(0)} + \lambda \psi_i^{(1)} \\ &= \psi_i^{(0)} + \lambda \sum_{j\neq i} \frac{\langle \psi_i^{(0)} \mid V \mid \psi_j^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} \psi_j^{(0)} \end{aligned} \tag{5.28b}$$

Equation (5.28b) cannot be valid if there is a degeneracy in the eigenspectrum of $\hat{H}^{(0)}$, i.e., $E_i^{(0)} = E_j^{(0)}$ for $i \neq j$.

We shall seek a more explicit expression for the second-order energy. The second order correction to the energy of the eigenfunction ψ_i is given by (Eq. 5.15).

$$E_i^{(2)} = \langle \psi_i^{(0)} \mid V \mid \psi_i^{(1)} \rangle \tag{5.29}$$

Substituting for $\psi_i^{(1)}$ from Eq. (5.27), in Eq. (5.29) we have,

$$E_i^{(2)} = \sum_{j\neq i} \frac{\langle \psi_j^{(0)} \mid V \mid \psi_i^{(0)} \rangle \langle \psi_i^{(0)} \mid V \mid \psi_j^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} = \sum_{j\neq i} \frac{V_{ji}V_{ij}}{E_i^{(0)} - E_j^{(0)}} \tag{5.30}$$

where

$$V_{ij} = \langle \psi_i^{(0)} \mid V \mid \psi_j^{(0)} \rangle \tag{5.31}$$

Because of the hermitian property of V, $(V_{ij}.\ V_{ji})$ is real and positive. It is seen from Eqs. (5.28b) and (5.30) that the first-order correction to the coefficients and the second-order correction to the energy involve the energy difference between two zero-order states in the denominator. Therefore, the zero-order states which have the largest effect on ψ_i are those which are closest in energy to $\psi_i^{(0)}$.

As we have earlier mentioned, since the perturbation theory is applicable to a system which is only slightly different from the unperturbed one, it is rarely necessary to go to higher-order terms. However, the fact remains that this form of the theory is not valid if there are degenerate zero-order states. The systems having degenerate states can be treated by using a modification of the variation method which will be described later in this chapter.

5.3 An Example of the Application of Perturbation Method

Let $\hat{H}_0$ be the hamiltonian operator for a hydrogen atom and $\psi_0^{(0)}$, $\psi_1^{(0)}, \psi_2^{(0)}$ . . . etc. be its eigenfunctions. When a uniform electric field along Z-axis is applied, the perturbation term V is given by (since λ is an arbitrary parameter, it is chosen to have the value unity):

$$V = eFZ = eFr \cos \theta \text{ (in spherical polar coordinate)} \tag{5.32}$$

which is to be added to $\hat{H}^{(0)}$, where e is the electronic charge, and F, the strength of the applied field. The energy of the ground state of the hydrogen atom which is non-degenerate is given by the following expression which is correct to the second order:

$$\begin{aligned} E_0 &= E_0^{(0)} + E_0^{(1)} + E_0^{(2)} \\ &= E_0^{(0)} + eF \langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_0^{(0)} \rangle + e^2F^2 \sum_{j\neq 0} \frac{\langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_j^{(0)} \rangle^2}{E_0^{(0)} - E_j^{(0)}} \\ &= E_0^{(0)} + F\cdot\langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_0^{(0)} \rangle + F^2 \sum_{j\neq 0} \frac{\langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_j^{(0)} \rangle^2}{E_0^{(0)} - E_j^{(0)}} \\ &\qquad \text{[in a.u.]} \end{aligned} \tag{5.33}$$

The ground state of the hydrogen atom is represented by 1s orbital whose wave function is

$$\psi_0^{(0)} = \frac{1}{\sqrt{\pi}} \exp(-r) \tag{5.34}$$

The integral

$$\langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_0^{(0)} \rangle = \frac{1}{\pi} \int_0^\infty \exp(-2r) r^3 \, dr \int_0^\pi \sin\theta \cos\theta \, d\theta \times \int_0^{2\pi} d\phi = 0 \tag{5.35}$$

since

$$\int_0^\pi \sin\theta \cos\theta \, d\theta = 0 \tag{5.36}$$

Thus, there is no first order effect on the ground state. However, this perturbation may cause a second order effect owing to the mixing of $\psi_0^{(0)}$ with certain appropriate excited states. The excited states which lie closest to $\psi_0^{(0)}$ in energy are the $2s$, $2p_x$, $2p_y$ and $2p_z$ states which are fourfold degenerate. Of these four states, only the interaction between $1s$ and $2p_z$ orbitals are non-vanishing while the other interactions vanish because the angular parts of the integral are zero. The integral between $1s$ and $2p_z$ hydrogenic orbitals is

$$\langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_j^{(0)} \rangle = \langle 1s \mid r\cos\theta \mid 2p_z \rangle$$

$$= \frac{1}{\pi}\,\frac{1}{4\sqrt{2}} \int_0^\infty \exp(-3r/2) r^4\, dr \int_0^\pi \sin\theta \cos^2\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \left(\frac{2}{3}\right)^5 2^3/\sqrt{2}$$

(see Eq. 5.57)

where

$$2p_z = \psi_j^{(0)} = \frac{1}{4\sqrt{2\pi}} \exp(-\tfrac{1}{2}r) r \cos\theta \tag{5.37}$$

In classical physics, the energy of an atom in the presence of a uniform static electric field F is given by

$$E_0 = E_0^{(0)} + \tfrac{1}{2}\alpha F^2 \tag{5.38}$$

where $E_0^{(0)}$ is the energy in the absence of the field and α is called the polarisability. On comparing this equation with (5.33) we find for the polarisability of the hydrogen atom

$$\alpha = 2\cdot \sum_{j\neq 0} \frac{\langle \psi_0^{(0)} \mid r\cos\theta \mid \psi_j^{(0)} \rangle^2}{E_0^{(0)} - E_j^{(0)}} \tag{5.39}$$

since the first-order term in Eq. (5.33) is zero.

5.4 The Variation Theorem

If we can make a guess of an approximate wave function of a system based on the physical and chemical considerations intuitively, then the energy of the system is approximately given by

$$E = \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \tag{5.40}$$

If the chosen function ψ is normalised then E can be written as

$$E = \langle \psi \mid H \mid \psi \rangle \tag{5.41}$$

where $\hat{H}$ is the complete hamiltonian of the system. The energy E, according to the variation theorem which will be proved shortly is always greater than the true energy E_0 (or the lowest eigenvalue of $\hat{H}$) of the system in its ground state. In other words, if we make several guesses of wave functions, say, ψ_1 and ψ_2 which lead to E_1 and E_2 respectively according to Eq. (5.40) or (5.41) then, in accordance with the variation principle, if $E_1 < E_2$, E_1 is the better approximation to the true energy E_0 than E_2. Therefore, the corresponding wave function ψ_1 is a better wave function of the system than ψ_2.

The variation theorem may thus be stated as follows: If ψ be the trial wave function of a system whose hamiltonian $\hat{H}$ has a discrete eigen spectrum, then

$$\langle \psi \mid H \mid \psi \rangle \geqslant E_0 \tag{5.42}$$

where E_0 is the lowest exact eigenvalue of $\hat{H}$ assuming that the trial wave function ψ is normalised.

Proof: Let ϕ_0, ϕ_1, ϕ_2, ϕ_3, . . . be the set of normalised and mutually orthogonal eigenfunctions of $\hat{H}$ with discrete eigenvalues such as E_0, E_1, E_2, E_3, etc., respectively. Thus

$$\hat{H}\phi_i = E_i\phi_i \qquad i = 0, 1, 2, 3, \ldots \tag{5.43}$$

To prove the theorem we expand ψ in terms of this set of eigenfunctions,

$$\psi = \sum_i C_i\phi_i \tag{5.44}$$

Since $\langle \psi \mid \psi \rangle = 1$, we have

$$\sum_i C_i^2 = 1 \tag{5.45}$$

Moreover,

$$\langle \phi_i \mid H \mid \phi_i \rangle = E_i \tag{5.46}$$

and

$$\langle \phi_i \mid H \mid \phi_j \rangle = E_j \langle \phi_i \mid \phi_j \rangle = 0 \tag{5.47}$$

Consider the integral

$$\begin{aligned} E = \langle \psi \mid H \mid \psi \rangle &= \langle \sum_i C_i\phi_i \mid H \mid \sum_j C_j\phi_j \rangle \\ &= \sum_i C_i^2 \langle \phi_i \mid H \mid \phi_i \rangle + \sum_{i \neq j} C_iC_j \langle \phi_i \mid H \mid \phi_j \rangle \end{aligned} \tag{5.48}$$

But the second summation vanishes owing to (5.47). Therefore,

$$E = \sum_i C_i^2 E_i \tag{5.49}$$

If E_0 be the lowest eigenvalue of $\hat{H}$, then one can write

$$\begin{aligned} E - E_0 &= \sum_i C_i^2 E_i - E_0 \\ &= \sum_i C_i^2 E_i - \sum_i C_i^2 E_0 \qquad \text{(from Eq. 5.45)} \\ &= \sum_i C_i^2 (E_i - E_0) \end{aligned} \tag{5.50}$$

The quantity $(E_i - E_0)$ must be positive or zero for all values of i and since C_i^2 is always positive it is seen that the right hand side of Eq. (5.50) must be always positive or zero. It follows

$$(E - E_0) \geqslant 0$$

or
$$\langle \psi \mid H \mid \psi \rangle \geqslant E_0 \tag{5.51}$$

In other words, if the trial wavefunction ψ happens to be the true wave function of the system in its lowest energy state, we get true energy E_0. Otherwise, the variation method always gives an upper bound to the true energy without giving any indication how far the true energy is different from the calculated value.

The application of the variation method involves the following steps:

1. Choose a trial function ψ with some variable parameters.
2. Calculate the integral $\langle \psi \mid H \mid \psi \rangle$
3. Since this integral always gives an upper bound to the true energy unless the chosen function ψ happens to be the exact one, minimise the integral with respect to the variable parameters.
4. The function ψ with the optimum value of the parameters is the best approximation of its class to the true wavefunction and the lowest value of $\langle \psi \mid H \mid \psi \rangle$ is the nearest approximation to the true energy, for all trial wave functions belonging to the same class.

5.5 An Example of the Application of the Variation Method

We shall illustrate the application of the variation method to a simple case for which the Schrödinger equation is exactly solvable. The purpose of choosing such an example is to show how powerful is the variation method and the extent to which the results of the variation method differ from the exact values. As an example, let us consider again the hydrogen atom for which the hamiltonian operator (in atomic units) is

$$\hat{H} = -\tfrac{1}{2}\nabla^2 - 1/r \tag{5.52}$$

where ∇^2 in spherical polar coordinates is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{5.53}$$

From physical intuition one can say that a system like the hydrogen atom is spherically symmetrical. The wavefunction of its lowest state must be spherically symmetrical because the wavefunction must have no nodes. One can choose a wave function of the form

$$\psi = \exp(-\gamma \cdot r) \tag{5.54}$$

where γ is a variable parameter. Since the function is spherically symmetrical both $\partial\psi/\partial\theta$ and $\partial\psi/\partial\phi$ must vanish. Thus, $\hat{H}\psi$ becomes

$$\hat{H}\psi = -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\exp(-\gamma\cdot r)\right] - \frac{1}{r}\exp(-\gamma\cdot r)$$

$$= \left[-\frac{1}{2}\left(\gamma^2 - \frac{2\gamma}{r}\right) - \frac{1}{r}\right]\exp(-\gamma\cdot r) \tag{5.55}$$

The energy is given by

$$E = \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle}$$

$$= \frac{\int_0^\infty \exp(-\gamma\cdot r)\left[-\frac{1}{2}\left(\gamma^2 - \frac{2\gamma}{r}\right) - \frac{1}{r}\right]\exp(-\gamma\cdot r)r^2\,dr \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi}{\int_0^\infty \exp(-2\gamma\cdot r)\,r^2\,dr \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi}$$

$$= \frac{-\frac{\gamma^2}{2}\int_0^\infty \exp(-2\gamma r)r^2\,dr + \gamma\int_0^\infty \exp(-2\gamma r)\,r\,dr - \int_0^\infty \exp(-2\gamma r)r\,dr}{\int_0^\infty \exp(-2\gamma\cdot r)r^2\,dr} \tag{5.56}$$

We use the following standard integral to evaluate the integrals in Eq. (5.56)

$$\int_0^\infty \exp(-ax)x^n\,dx = \frac{n!}{a^{n+1}} \tag{5.57}$$

Thus,

$$E = \frac{-\frac{\gamma^2}{2}\cdot\frac{2}{(2\gamma)^3} + \gamma\frac{1}{(2\gamma)^2} - \frac{1}{(2\gamma)^2}}{2/(2\gamma)^3}$$

$$= \left[\frac{\gamma^2}{2} - \gamma\right] \tag{5.58}$$

The condition that E be minimum is

$$\frac{\partial E}{\partial \gamma} = \gamma - 1 = 0 \quad \text{or} \quad \gamma = 1 \tag{5.59}$$

So that the lowest eigenvalue is

$$E = -\tfrac{1}{2}\ (\text{a.u.}) \tag{5.60}$$

and the corresponding eigenfunction is

$$\psi = \exp(-r) \tag{5.61}$$

These represent the exact eigenvalue and eigenfunction of the hydrogen atom in its ground state. The fact that these results are identical with the exact solution of the Schrödinger equation is due fortunately, to the well chosen form of our trial function. We might have chosen a function of the form

$$\psi = \exp(-\gamma r^2) \tag{5.62}$$

which led to the expectation value,

$$E = -0.424 \text{ a.u.} \tag{5.63}$$

slightly higher than the exact value. In fact it is possible to give a greater flexibility to the trial function such as

$$\psi = \exp(-\gamma r^n) \tag{5.64}$$

where γ and n are parameters. By minimising the energy with respect to γ and n one can obtain the following optimum values of these parameters

$$n = 1, \qquad \gamma = 1$$

The only significance that can be attached to this result is that by choosing a trial function of the right form one can hopefully obtain a fairly good approximation to the true energy by the variation method.

5.6 Application of the Variation Method to Other States

Although the variation method is primarily important for ground states, it can be used to a limited extent, for the calculation of the energy levels and eigenfunctions for the excited states. The wavefunction of the lowest state of hydrogen atom is spherically symmetrical but there are other wave functions which are not spherically symmetric and have characteristic nodal surfaces. For example, the $2p_z$ orbital has the X–Y plane as a nodal plane. If we can appropriately choose a second trial function which is orthogonal to the one chosen for the ground state and carry out the same procedure as described above we will obtain an approximation to the energy of the lowest p-state. By a similar argument one can determine the energy of the lowest d-state of an atom, etc. Thus the variation method can be used to determine the energies of the lowest states corresponding to each symmetry type.

5.7 Time-dependent Perturbation Theory

This section will be concerned with the time-dependent phenomena. In Chapter 2 we have learned that if $\hat{H}$ is independent of time, then the wave function can be factorised into two functions [Eq. (2.71)]:

$$\psi(r, t) = \psi(r) \cdot \exp\left(-\frac{2\pi i}{h} Et\right) \tag{5.65}$$

If $\hat{H}$ is time-dependent, this factorisation is not valid. We then face a difficult problem of finding the solution of the Schrödinger equation

$$\frac{ih}{2\pi} \frac{\partial \psi}{\partial t} = \hat{H}\psi \tag{5.66}$$

The time-dependent perturbation theory provides an approximation technique of finding a reasonable solution to Eq. (5.66). The basic ideas on which this theory is based are similar to that described under the general time-independent perturbation theory.

We assume that the hamiltonian of a system can be divided into two parts

$$\hat{H} = \hat{H}^0(r) + \hat{V}(r, t) \tag{5.67}$$

where $\hat{H}^0$ is the unperturbed time-independent hamiltonian whose wave functions describe the stationary states of the unperturbed system; $\hat{V}(r, t)$ is a very small perturbation that depends on both space (r) and time (t) variables such that

$$| \hat{H}^0(r) | \gg | \hat{V}(r, t) |$$

Since the total hamiltonian $\hat{H}(r, t)$ is time-dependent, the energy cannot be conserved so that there are no stationary states. The problem now is to find the wave function of $\hat{H}(r, t)$ from those of the stationary states of the unperturbed system whose hamiltonian is $\hat{H}^0(r)$.

The eigenfunctions of $\hat{H}^0(r)$ are the solutions of the equation

$$\frac{ih}{2\pi} \frac{\partial \psi_i^0(r, t)}{\partial t} = \hat{H}^{(0)}(r)\psi_i^{(0)}(r, t) \tag{5.68}$$

It is presumed that the set of eigenfunctions, i.e. $\psi_i^{(0)}(r, t)$, $\psi_j^{(0)}(r, t)$, etc. of Eq. (5.68) are known and they must be written in their time-dependent form:

$$\psi_i^{(0)}(r, t) = \psi_i^{(0)}(r) \exp\left(-\frac{2\pi i}{h} E_i^{(0)} t\right) \tag{5.69}$$

where $\psi_i^{(0)}(r)$ is independent of time and $E_i^{(0)}$ is the eigenvalue of $\hat{H}^0$. The equation to be solved is

$$[\hat{H}^0(r) + \hat{V}(r, t)]\, \psi_i(r, t) = \frac{ih}{2\pi} \frac{\partial \psi_i}{\partial t}(r, t) \tag{5.70}$$

We shall attempt to find the solution of Eq. (5.70) by expanding $\psi_i(r, t)$ in terms of the complete set of the unperturbed time-dependent functions of the form (5.69) since the latter form a complete orthonormal set. Thus

$$\psi_i(r, t) = \sum_k a_{ik}(t)\psi_k^{(0)}(r, t) \tag{5.71}$$

where the coefficients of mixing, i.e. a_{ik} are also functions of time. This expansion means that before the perturbation was applied the system was represented by a pure state $\psi_i^0(r, t)$. After the perturbation is imposed the system is described by a mixture of the unperturbed states. Since the coefficients of mixing varies with time, as time proceeds, the function is described by different mixtures. It may happen that at a later time the mixture of states actually represents either predominantly or completely another pure unperturbed state, say $\psi_f^0(r, t)$. We will now seek to find the coefficient of mixing with $\psi_f^0(r, t)$ in the expansion in Eq. (5.71). If Eq. (5.71) is inserted in (5.70) we have

$$\sum_k a_{ik}(t)\hat{H}^{(0)}(r)\psi_k^{(0)}(r, t) + \sum_k a_{ik}(t)\hat{V}(r, t)\psi_k^{(0)}(r, t)$$

$$= \frac{ih}{2\pi} \sum_k \frac{\partial a_{ik}(t)}{\partial t} \psi_k^{(0)}(r, t) + \frac{ih}{2\pi} \sum_k a_{ik}(t) \frac{\partial \psi_k^{(0)}(r, t)}{\partial t} \tag{5.72}$$

We assume that V does not involve $\partial/\partial t$. In view of Eq. (5.68), the first term on the left hand side of Eq. (5.72) cancels with the second term on its right hand side. We, therefore, have

$$\sum_k a_{ik}(t)\hat{V}(r, t)\psi_k^{(0)}(r, t) = \frac{ih}{2\pi} \sum_k \frac{\partial a_{ik}(t)}{\partial t} \psi_k^{(0)}(r, t) \tag{5.73}$$

Multiplying both sides with $\psi_f^0(r, t)$ and integrating

$$\sum_k a_{ik}(t) \langle \psi_f^{(0)}(r, t) \mid V(r, t) \mid \psi_k^{(0)}(r, t) \rangle$$

$$= \frac{ih}{2\pi} \sum_k \frac{\partial a_{ik}}{\partial t} \langle \psi_f^{(0)}(r, t) \mid \psi_k^{(0)}(r, t) \rangle \tag{5.74}$$

Since, $\psi_k^0(r, t)$, $\psi_f^0(r, t)$, etc. are orthonormal, i.e.

$$\langle \psi_f^{(0)}(r, t) \mid \psi_k^{(0)}(r, t) \rangle = \delta_{fk}$$

all the terms in the summation of the right hand side of Eq. (5.74) vanish except the one for which $f = k$. One obtains

$$\frac{\partial a_{if}(t)}{\partial t} = \frac{2\pi}{ih} \sum_k a_{ik}(t) \langle \psi_f^{(0)}(r, t) \mid V(r, t) \mid \psi_k^{(0)}(r, t) \rangle \tag{5.75}$$

We shall now introduce certain approximations. As the perturbation $\hat{V}$ is small, the rate of change of the coefficients a_{if} is also small. It is zero when the perturbation is absent. Initially the system is described by a pure state $\psi_i(r, t)$. Therefore, when $t = 0$, $a_{ii}(0) = 1$ and a_{ii} continues to be nearly equal to unity for a short while after $t = 0$, while all other coefficients a_{ik} are neglected in comparison with a_{ii}. The only important term in the summation of Eq. (5.75) is the one having $k = i$ and we can write

$$\frac{\partial a_{if}(t)}{\partial t} = \frac{2\pi}{ih} \langle \psi_f^{(0)}(r, t) \mid V_{(r, t)} \mid \psi_i^{(0)}(r, t) \rangle$$

$$a_{if}(t) - a_{if}(0) = \frac{2\pi}{ih}\int_0^t \langle \psi_f^{(0)}(r, t) \mid V(r, t) \mid \psi_i^{(0)}(r, t) \rangle dt \tag{5.76}$$

If we use the time-dependent form (5.69) of $\psi_f^0(r, t)$ and $\psi_i^0(r, t)$ we then have

$$a_{if}(t) - a_{if}(0) = \frac{2\pi}{ih} \int_0^t V_{fi}(t) \exp\left[\frac{2\pi i}{h}(E_f^{(0)} - E_i^{(0)})\,t\right] dt \tag{5.77}$$

where $$V_{fi}(t) = \langle \psi_f^{(0)}(r) \mid V(t) \mid \psi_i^{(0)}(r) \rangle \tag{5.78}$$

But according to our assumption $a_{if}(0) = 0$; the value of a_{if} after time t is given by

$$a_{if} = \frac{2\pi}{h}\int_0^t V_{fi}(t)\exp\left[\frac{2\pi i}{h}(E_f^{(0)} - E_i^{(0)})t\right]dt \tag{5.79}$$

This equation yields a_{if} and $|a_{if}|^2$ may be interpreted as measuring the probability that a given perturbation carried the system from the stationary state $\psi_i^0(r)$ to the stationary state $\psi_f^0(r)$.

5.8 Harmonic Perturbation and Transition Probabilities

There are various ways the perturbation may be applied. However, we shall discuss only the harmonic perturbation which results when atoms or molecules are exposed to the electromagnetic radiation. The electromagnetic field of the radiation is represented by an oscillating electric field ϵ and an oscillating magnetic field **H** perpendicular to each other and to the direction of propagation of the waves. They have equal magnitude provided ϵ is measured in electrostatic units and **H** in electromagnetic units. However, the interaction of the electromagnetic radiation with electrons or any charged particle of the matter will be due, mainly to the electric field associated with the radiation rather than its magnetic field. This is because the force exerted on a particle of charge e by the electric field is $e\epsilon$ while the force exerted on the same particle by a magnetic field is evH/c where v is the velocity of the particle and c, the velocity of light. Since in most systems $v \ll c$, the magnetic contribution is much smaller than the electric contribution to the interaction.

The oscillating electric field associated with electromagnetic radiation of frequency ν is given by

$$\epsilon(\nu, t) = 2\epsilon_0(\nu)\cos 2\pi\nu t \tag{5.80}$$

where $2\epsilon_0(\nu)$ is the amplitude of $\epsilon(\nu, t)$. When an oscillating electric field interacts with a charged particle, it causes a displacement of the particle with the resultant creation of an instantaneous dipole moment, say er, where r is the displacement caused by the interaction. Since the molecular or atomic dimensions are of the order of a few angstroms while the wavelength of the U.V. or visible radiation is several thousand angstroms it may be reasonably assumed that the oscillation of electric field is constant over the space occupied by an atomic or a molecular system. Then the perturbation hamiltonian $\hat{V}$, i.e. the energy of interaction is given by

$$\begin{aligned} V &= er\cdot\epsilon(\nu, t) \\ &= 2e\epsilon_0(\nu)\cos 2\pi\nu t\cdot r \\ &= e[\exp(2\pi i\nu t) + \exp(-2\pi i\nu t)]\epsilon_0(\nu).r \end{aligned} \tag{5.81}$$

Let us consider the component of ϵ in the z-direction. This field, i.e. $\epsilon_0^z(\nu)$, can create a dipole in the z-direction. Equation (5.78) may now be written as

$$V_{fi}(t) = e[\exp(2\pi i\nu t) + \exp(-2\pi i\nu t)]\epsilon_0^z(\nu) \langle \psi_f^{(0)}(r) \mid z \mid \psi_i^{(0)}(r) \rangle$$
$$= [\exp(2\pi i\nu t) + \exp(-2\pi i\nu t)]\epsilon_0^z(\nu)\cdot z_{if} \tag{5.82}$$

where $z_{if} = e\langle \psi_f^{(0)}(r) \mid z \mid \psi_i^{(0)}(r) \rangle$ (5.83)

The integral z_{if} is called the component of the transition dipole moment in the z-direction. Equation (5.79) may now be written as

$$a_{if} = \frac{2\pi}{ih}\left[\epsilon_0^z(\nu).z\cdot_{if}\right]\left\{\int_0^t \exp[2\pi i(\nu_{fi} + \nu)t]\,dt + \int_0^t \exp[2\pi i(\nu_{fi} - \nu)t]\,dt\right\} \tag{5.84}$$

where $\nu_{fi} = (E_f^0 - E_i^0)/h$ (5.85)

Equation (5.84) on integration gives

$$a_{if} = \frac{2\pi}{ih}[\epsilon_0^z(\nu)\cdot z_{if}]\left\{\frac{\exp[2\pi i(\nu_{fi} + \nu)t] - 1}{2\pi i(\nu_{fi} + \nu)} + \frac{\exp[2\pi_i(\nu_{fi} - \nu)t] - 1}{2\pi i(\nu_{fi} - \nu)}\right\} \tag{5.86}$$

The terms inside the second bracket of (5.86) are very small unless the denominators are small. This is possible when ν_{fi} and ν are of the same order of frequencies. For $\nu_{fi} = \nu$, the situation is referred to as the resonance condition when the perturbation is most efficacious. Thus in an absorption process, $E_f > E_i$ the first term of Eq. (5.86) can be neglected in comparison with the second term which will become appreciable only for

$$\nu = \nu_{fi}$$

Similarly, in an emission process $E_f < E_i$, the second term is neglected and the first term becomes appreciable if

$$\nu \approx \nu_{fi}$$

In dealing with the absorption phenomenon, we neglect the first term. Therefore, the probability of finding the system in a stationary state $\psi_f^{(0)}$ at time t if initially ($t = 0$) it was in a stationary state $\psi_i^{(0)}$, is given as[2]

$$|a_{if}|^2 = a_{if}^* a_{if} = \frac{4\pi^2}{h^2} |\epsilon_0^z(\nu)|^2 \cdot |z_{if}|^2 \times \left| \frac{\exp[2\pi i(\nu_{fi} - \nu)t] - 1}{2\pi i(\nu_{fi} - \nu)} \right|^2$$
$$= \frac{4}{h^2} |\epsilon_0^z(\nu)|^2 \, |z_{if}|^2 \left[\frac{\sin^2 \pi(\nu_{fi} - \nu)t}{(v_{fi} - \nu)^2}\right] \tag{5.87}$$

As we have already mentioned, $|a_{if}|^2$ is significant only when $\nu_{fi} \approx \nu$. In a real experiment one employs a perturbation field which spans a range of

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[2] Use is made of the following relation:

$$|\exp(i\theta) - 1|^2 = [\exp(i\theta) - 1][\exp(-i\theta) - 1]$$
$$= 2 - 2\cos\theta = 2[1 - \cos 2\cdot\theta/2]$$
$$= 2[1 - \cos^2\theta/2 + \sin^2\theta/2] = 4\sin^2\theta/2$$

frequencies. So, we must integrate the right hand side of Eq. (5.87) over the range of frequencies. However, only a narrow range of frequencies around the resonance frequency makes a non-negligible contribution to $|a_{if}|^2$. This becomes evident from Fig. 5.1.

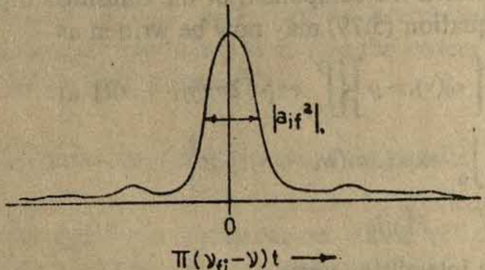

Fig. 5.1 *The dependence of* $|a_{if}|^2$ *on the frequency of the perturbing field.*

We may, therefore, assume that $\epsilon_0^z(\nu)$ does not change very much over the range of frequencies and may be taken outside the integral. However, the limits of integration may be extended from a small range to ± ∞ without invoking any serious error but with an advantage of having the integral in a standard form. One may write

$$|a_{if}|^2 = \frac{4}{h^2}\,|\epsilon_0^z(\nu)|^2\,|z_{if}|^2 \int_{-\infty}^{+\infty} \frac{\sin^2 \pi(\nu_{fi}-\nu)t}{(\nu_{fi}-\nu)^2}\,d\nu \tag{5.88}$$

Let us assume

$$\pi(\nu_{fi}-\nu)t = \theta$$

then,

$$\nu_{fi}-\nu = \theta/t\pi$$

or

$$-d\nu = d\theta/t\pi$$

The integral in Eq. (5.88) becomes

$$\int_{-\infty}^{\infty} \frac{\sin^2 \pi(\nu_{fi}-\nu)t}{(\nu_{fi}-\nu)^2}\,d\nu = t\pi \int_{-\infty}^{\infty} \frac{\sin^2\theta}{\theta^2}\,d\theta = t\pi^2 \tag{5.89}$$

where the use is made of the following standard integral

$$\int_{-\infty}^{+\infty} \frac{\sin^2\theta}{\theta^2}\,d\theta = \pi$$

Therefore Eq. (5.88) becomes

$$|a_{if}|^2 = \frac{4\pi^2}{h^2}\,|\overset{z}{\epsilon_0}(\nu)|^2\,|z_{if}|^2 t \tag{5.90}$$

So, we see that the transition $i \rightarrow f$ occurs with a probability that is proportional to the square of the transition dipole moment between the initial and final states. It is also important to note that the probability increases linearly with time.

In a real experiment one may not be concerned with a transition to a perfectly defined state, instead one observes transitions to a range of states. Then, the probability of transitions to a range of states will be the sum of the probabilities in Eq. (5.90). Thus the total probability of transition is

$$P(t) = \sum_f |a_{if}|^2 \tag{5.91}$$

where the sum ranges over the states f. Since the final states f may occur as a narrow band of levels within a frequency range ν_f and $\nu_f + d\nu_f$ we may introduce the number density of final states. Let us call this density of final states, $n(\nu_f)$. We may reasonably assume that $n(\nu_f)$ does not change much in the significant but narrow range of frequencies about the resonance frequency (Fig. 5.1). The total probability of transitions to a band of levels is approximately given by

$$P(t) = |a_{if}|^2 n(\nu_f)$$

or

$$P(t) = \frac{4\pi^2}{h^2} |\epsilon_0^z(\nu)|^2 |z_{if}|^2 t n(\nu_f) \tag{5.92}$$

The constant transition rate to a narrow band of levels may be given as

$$\omega_{i\to f} = \frac{P(t)}{t} = \frac{4\pi^2}{h^2} |\epsilon_0^z(\nu)|^2 |z_{if}|^2 n(\nu_f) \tag{5.93}$$

It is however more common to express the density of states as the number of states in an energy range rather than the frequency range. Let $dN(\nu_f)$ be the number of final states in an energy range E and $E + dE$. The new density of states $\rho(\nu_f)$ is given by

$$\rho(\nu_f) = \frac{dN(\nu_f)}{dE} = \frac{dN(\nu_f)}{h d\nu_f} = \frac{n(\nu_f)}{h} \tag{5.94}$$

where the energy of a state ψ_f^0 is expressed as $h\nu_f$.
Therefore,

$$\omega_{i\to f} = \frac{4\pi^2}{h} |\epsilon_0^z(\nu)|^2 |z_{if}|^2 \rho(\nu_f) \tag{5.95}$$

For the three-dimensional case we have

$$\omega_{i\to f} = \frac{4\pi^2}{h} |\epsilon_0(\nu)|^2 |r_{if}|^2 \rho(\nu_f) \tag{5.96}$$

where

$$|\epsilon_0(\nu)|^2 = |\epsilon_0^z(\nu)|^2 + |\epsilon_0^y(\nu)|^2 + |\epsilon_0^x(\nu)|^2$$

$$|r_{if}|^2 = |z_{if}|^2 + |y_{if}|^2 + |x_{if}|^2$$

Equation (5.96) is known as Fermi's Golden Rule.

5.9 The Einstein Transition Probabilities

According to the classical electromagnetic theory, the radiation density $\rho(\nu)\,d\nu$ in the frequency range ν and $\nu + d\nu$ is given by

$$\rho(\nu)\,d\nu = \frac{\overline{\epsilon^2(\nu, t)}}{4\pi} \tag{5.97}$$

where the bar over $\epsilon^2(\nu, t)$ indicates its average value. If we assume the radiation to be isotropic, i.e. the x-, y- and z-components of its electric field are the same, then

$$\overline{|\epsilon^z(\nu, t)|^2} = \overline{|\epsilon^y(\nu, t)|^2} = \overline{|\epsilon^x(\nu, t)|^2} = \tfrac{1}{3}\,\overline{|\epsilon(\nu, t)|^2}$$

and the radiation density is then given by

$$\rho(\nu)\,d\nu = \frac{3}{4\pi}\,\overline{|\epsilon^z(\nu, t)|^2} \tag{5.98}$$

From Eq. (5.80)

$$\begin{aligned}\overline{|\epsilon^z(\nu, t)|^2} &= \overline{|2\epsilon_0^z \cos 2\pi\nu t|^2} = 4\,\overline{|\epsilon_0^z(\nu)|^2 \cos^2 2\pi\nu t}\\ &= 2\,\overline{|\epsilon_0^z(\nu)|^2}\end{aligned} \tag{5.99}$$

since the average value of $\cos^2\theta$ is 1/2. Therefore, Eq. (5.98) is now written as

$$\rho(v)\,dv = \frac{6}{4\pi}\,|\overline{\epsilon_0^z(\nu)}|^2 \tag{5.100}$$

The transition is a consequence of the interaction of the electromagnetic field of the radiation with the electrons of atoms or molecules. The probability of transition from a well defined state ψ_i^0 to another well defined state ψ_f^0 is given by

$$\begin{aligned}|a_{if}|^2 &= B_{if}\,\rho(\nu)\,d\nu \cdot t\\ &= B_{if}\frac{6}{4\pi}\,\overline{|\epsilon_0^z(\nu)|^2}\cdot t\end{aligned} \tag{5.101}$$

Since no transitions occur unless the radiation contains the transition frequency, the proportionality constant B_{if} is known as Einstein's coefficient of stimulated absorption. Comparing Eq. (5.90) with (5.101) one obtains, for radiations polarised in the Z-direction,

$$B_{if} = \frac{8\pi^3}{3h^2}\,|z_{if}|^2 \tag{5.102}$$

For the general case

$$\begin{aligned}B_{if} &= \frac{8\pi^3}{3h^2}[\,|z_{if}|^2 + |y_{if}|^2 + |x_{if}|^2]\\ &= \frac{8\pi^3}{3h^2}\,|r_{if}|^2\end{aligned} \tag{5.103}$$

It is easy to see that the transition probability for the inverse processes, i.e. emission is the same as that for absorption. Einstein introduced the coefficient of stimulated emission, i.e. B_{fi} and

$$B_{if} = B_{fi} \tag{5.104}$$

However, the excited atoms or molecules emit radiation even in the absence of an external electromagnetic field. Einstein, therefore, introduced a coefficient of spontaneous emission A_{fi}, independent of radiation density. We shall now find a relation between A_{fi} and B_{if}.

Consider a system of atoms or molecules in equilibrium with radiation. Let N_i be the number of atoms (or molecules) in the state ψ_i^0 and N_f in the state ψ_f^0 at equilibrium, and let us assume that $\rho(\nu_{fi})$ be the equilibrium density of radiation of the transition frequency, ν_{fi}. The number of atoms (or molecules) undergoing transition $i \rightarrow f$ is given by

$$N_i B_{if} \rho(\nu_{fi})$$

The number of atoms (or molecules) undergoing transition $f \rightarrow i$

$$N_f[A_{fi} + B_{fi}\rho(\nu_{fi})]$$

At equilibrium, they must be equal, i.e.

$$\frac{N_i}{N_f} = \frac{A_{fi} + B_{fi}\,\rho(\nu_{fi})}{B_{if}\,\rho(\nu_{fi})} \tag{5.105}$$

If thermal equilibrium is established, the Maxwell-Boltzmann distribution law applies. Therefore,

$$\frac{N_i}{N_f} = \frac{\exp(-E_i/kT)}{\exp(-E_f/kT)} = \exp\left(\frac{h\nu_{fi}}{kT}\right) \tag{5.106}$$

Since $B_{fi} = B_{if}$, combining Eqs. (5.105) and (5.106) one obtains

$$\rho(\nu_{fi}) = \frac{A_{fi}}{B_{if}}\left\{\exp\left(\frac{h\nu_{fi}}{kT}\right) - 1\right\}^{-1} \tag{5.107}$$

This equation clearly shows that $A_{fi} \neq 0$, otherwise the radiation density would be zero.

Planck's black body radiation formula for the radiation density is given as

$$\rho(v_{fi}) = \frac{8\pi h\nu_{fi}^3}{c^3}\left\{\exp\left(\frac{h\nu_{fi}}{kT}\right) - 1\right\}^{-1} \tag{5.108}$$

where c is the velocity of light. Comparison of Eq. (5.108) with Eq. (5.107) gives

$$A_{fi} = \frac{8\pi h\nu_{fi}^3}{c^3} B_{if} \tag{5.109}$$

Therefore, the coefficient for spontaneous emission for the electric dipole transitions is given by (following Eq. 5.103)

$$A_{fi} = \frac{8\pi h}{c^3}\,\nu_{fi}^3\,\frac{8\pi^3}{3h^2}\,|\,r_{if}\,|^2$$

$$= \frac{64}{3c^3}\,\frac{\pi^4}{h}\,\nu_{fi}^3\,|\,r_{if}\,|^2 \tag{5.110}$$

The important point that emerges from Eq. (5.110) is that the probability of spontaneous emission increases with the transition frequency and is very important at high frequencies. In this context, it would be of interest to compare the probability of the spontaneous infrared emission with that of the ultraviolet and visible emission. The infrared frequencies are in the range of 5000 $\text{cm}^{-1} \sim 1000\ \text{cm}^{-1}$ while the ultraviolet and visible bands occur around 30,000 cm^{-1}. Thus, ν_{fi}^3 of Eq. (5.110) for the infrared band are about 10^{-3} times that of the UV–visible bands. Besides, the vibrational transition dipoles are usually smaller than the transition dipoles for the electronic transitions. This fact introduces another order of magnitude of prohibition on the infrared emission. In this way, Eq. (5.110) explains why the spontaneous infrared emission is rarely observed under conditions where the UV–visible emissions are readily observable.

5.10 Lasers

For very large radiation densities, $B_{fi}\rho(\nu_{fi}) \gg A_{fi}$ in Eq. (5.105), it will then be reasonable to assume that $N_f \approx N_i$. If the population of the higher energy level, i.e., N_f is increased or the population of the lower energy level, i.e., N_i is decreased somehow such that $N_i/N_f < 1$, more photons of energy $h\nu_{fi}$ will be emitted than absorbed. If these emitted photons are in phase with the incident beam of same frequency, amplification of light can result. This process is known as light amplification by stimulated emission of radiation or in short, laser.

In order to achieve this amplification, the emitting materials (atoms or molecules) are kept in an optical cavity which is made up of a pair of parallel mirrors, one of which is semi-transparent (see Fig. 5.2) and the other is totally reflecting. These mirrors are separated by an integral number of $\frac{1}{2}\lambda$, where $E_f - E_i = hc/\lambda$. The light reflected from a mirror will be in phase with the incident beam. When the population inversion is achieved in the lasing material ($N_i < N_f$) contained in the optical cavity, a spontaneous emission

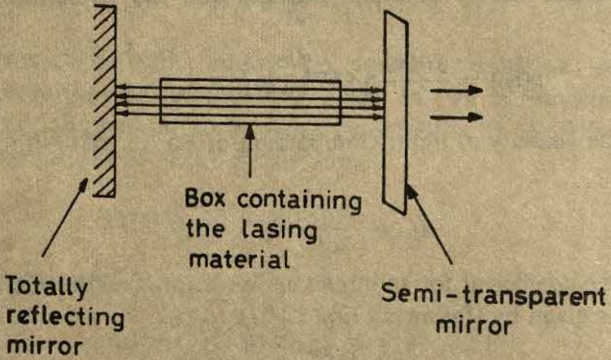

Fig. 5.2 *A schematic diagram for lasing action.*

provides a few photons of energy $h\nu_{fi}$. This radiation field will stimulate emission in other atoms or molecules, present in the optical cavity. The emitted light will be in phase with the incident beam. Thus, wave builds up in intensity as it travels back and forth between the two mirrors, and then escapes through the partially transparent mirror.

In order to achieve the nonequilibrium state, i.e., $N_i < N_f$ which is essential for laser action, an additional process is required or at least one other energy level must be involved. For example, suppose a state whose energy is E_m exists such that $E_m > E_f$ and its life time is short and its most probable spontaneous decay involves a transition to E_f rather than the E_i (see Fig. 5.3). We assume that E_f is a metastable state. It means that the probability of a spontaneous transition out of that state is very small, i.e., A_{fi} is small. Then a radiation of frequency $(E_m - E_i)/h$ can be used to pump atoms or molecules from the E_i state to the E_m state. Since the decay $E_m \rightarrow E_f$ is very fast, this process will increase the population of the state E_f relative to that of the state E_i.

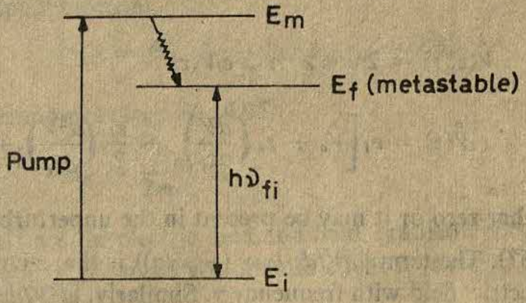

Fig. 5.3 *Energy level scheme for a three-level system*

More efficient than the above three-level system is the four-level system (see Fig. 5.4) where laser emission results from transition not to the ground state but to an unpopulated state. Let us call this state, E_i. If the state E_i which is populated by the transition $f \rightarrow i$ is also rapidly depopulated by a fast process to the ground state, E_o, it is then possible to maintain a continuous population inversion, i.e., $N_i/N_f < 1$. Such lasers will give a continuous light output. The Ne–Ne laser is an example of the four-level systems.

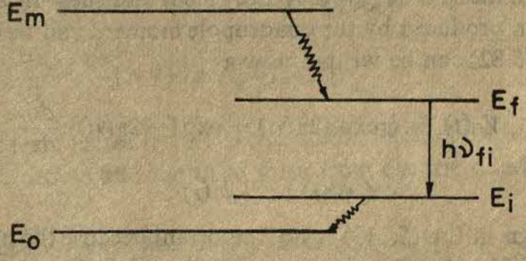

Fig. 5.4 *Energy level scheme for a four-level system*

The main characteristics of laser radiations besides its high intensity are (1) coherence, (2) high monochromaticity, because the optical cavity is tuned to one particular wavelength, so the light of other wavelengths is destroyed by interference.

5.11 Other Mechanisms of Transitions

In Sec. 5.8 we have assumed that wavelength of radiation that interacts with atoms or molecules is long compared with the atomic or molecular dimensions. Furthermore, the interaction of the oscillating magnetic field associated with the electromagnetic radiation has also been ignored. When we have an oscillating electric field, the field may not be same everywhere over the molecule.

Let us consider a simple one-dimensional case. The oscillating electric field of the radiation causes a displacement of the i^{th} charged particle of the atom (or molecule) in the z-direction by an amount z_i from the origin. The energy of interaction V or the perturbation hamiltonian $\hat{V}(z, t)$ may be given as

$$\hat{V}(z, t) = 2 \cos 2\pi\nu t \sum_i e_i \hat{V}(z) \tag{5.111}$$

where
$$e_i\hat{V}(z) = e_i\left[\hat{V}_o + z_i\left(\frac{dV}{dz_i}\right)_0 + \frac{z_i^2}{2}\left(\frac{d^2V}{dz_i^2}\right)_0 + \ldots\right] \tag{5.112}$$

$\hat{V}_0$ may be either zero or it may be present in the unperturbed hamiltonian $\hat{H}_0$ of Eq. (5.67). The term $| dV/dz_i |_0 = (-\epsilon_0^z(\nu))$ is the z-component of the oscillating electric field with frequency ν. Similarly, $|d^2V/dz_i^2|_0 = (-| d\epsilon_0^z/dz_i |_0)$ is the field gradient in the z-direction at the origin. Equation (5.112) can be written as

$$e_i\hat{V}(z) = -e_i\left[z_i\epsilon_0^z(\nu) + \frac{z_i^2}{2}\left(\frac{d\epsilon_0^z}{dz_i}\right)_0 + \ldots\right] \tag{5.113}$$

The first term of Eq. (5.113) gives rise to the z-component of the transition dipole moment. In Sec. 5.8 we did not consider the second term of Eq. (5.113). If we now consider this term in the perturbation hamiltonian $\hat{V}$ we obtain the z-z component of the transition quadrupole moment. Sometimes, the dipole moment integral z_{if} given by Eq. (5.83) vanishes. If it is so, then the weak radiation produced by the quadrupole moment can be observed. Thus, $V_{fi}(t)$ of Eq. (5.82) can be written now as

$$V_{fi}(t) = \tfrac{1}{2}[\exp(2\pi i\nu t) + \exp(-2\pi i\nu t)]\,\frac{d\epsilon_0^z}{dz_i}$$
$$\times \langle \psi_f^0(r) \mid z^2 \mid \psi^0(r) \rangle \tag{5.114}$$

The minus sign in Eq. (5.113) is not important because the probability of the transition $i \rightarrow f$ is always proportional to $| a_{if} |^2$. In Eq. (5.114) the integral

$\langle \psi_f^0(r) \mid z^2 \quad \psi_i^0(r) \rangle$ is called the transition quadrupole moment. In fact, Eq. (5.113) involves higher multipole terms and if the quadrupole term vanishes one has to consider the higher multipole terms in the expansion of Eq. (5.113).

Electromagnetic radiation has also an oscillating magnetic field, **H** associated with its time-dependent electric field $\epsilon_0(\nu)$. If m_α is the magnetic dipole of the moving charged particle in atoms (or molecules), then the hamiltonian describing an atom or molecule in such an external field may be written as[2]

$$\hat{H} = \hat{H}^0 - \mu_\alpha \epsilon_0^\alpha(\nu) - \frac{1}{3}\, \Theta_{\alpha\beta}\epsilon_0^{\alpha\beta} - m_\alpha H_0^\alpha \ldots \tag{5.115}$$

where $\hat{H}^0$ is the unperturbed hamiltonian of the atom or the molecule in the absence of the electromagnetic radiation, and electric dipole moment

$$\mu_\alpha = \sum_i e_i r_{i\alpha}$$

electric quadrupole moment

$$\Theta_{\alpha\beta} = \Theta_{\beta\alpha} = \tfrac{1}{2} \sum_i e_i(3 r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta})$$

magnetic dipole moment (see Eq. 4.95)

$$m_\alpha = \frac{e}{2m_e c}\, \hat{L}_\alpha$$

where ϵ_0^α and $\epsilon_0^{\alpha\beta}$ are the electric field and field gradient, H^α, the magnetic field at the origin; α, β denote vectors and equal to the x, y, z components. $\hat{L}_\alpha$ is the α-component of the orbital angular momentum vector. This operator need not apply only to orbital angular momentum but may also include spin.

The perturbation term $m_\alpha H_0^\alpha$ in Eq. (5.115) can give rise to magnetic dipole transition moment i.e., $\langle \psi_f^0(r) \mid \hat{L}_\alpha \mid \psi_i^0(r) \rangle$ which does not vanish for molecules in which total angular momentum is not conserved. If we include all three perturbation terms in the hamiltonian given by Eq. (5.115) then the Einstein coefficient for spontaneous emission is given by[3]

$$A_{fi} = \frac{64\pi^4}{3c^3 h} \nu_{fi}^3 \Big[|\langle \psi_f^0 | er | \psi_i^0 \rangle^2 + \left(\frac{e}{2m_e c}\right)^2 |\langle \psi_f^0 | \hat{L} | \psi_i^0 \rangle|^2 + \frac{3}{10}\pi^2 \frac{\nu_{fi}^3}{c^2} |\langle \psi_f^0 | err | \psi_i^0 \rangle|^2 \Big] \tag{5.116}$$

where the first term arises from electric dipole interaction, the second term from magnetic dipole and the third term from electric quadrupole interactions. We now estimate the relative orders of magnitude of these three terms disregarding the constant term.

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[2] A.D. Buckingham, *Adv. Chem. Phys.*, **12**, 107, (1967).

[3] E.U. Condon and G.H. Shortley, *Theory of Atomic Spectra*, p. 96, revised edition, Cambridge University Press, New York, (1950).

$$|\langle \psi_f^0 | er | \psi_i^0 \rangle|^2 \sim (ea_0)^2$$

$$\sim [4.8\times 10^{-10}\times 0.529\times 10^{-8}]^2$$

$$\sim 5.8\times 10^{-36}\ \text{cgs}$$

$$\left[\frac{e}{2m_e c}\langle \psi_f^0 | \hat{L} | \psi_i^0 \rangle\right]^2 \sim \left(\frac{eh}{4\pi m_e c}\right)^2$$

$$= (0.9274\times 10^{-20})^2$$

$$= 8.7\times 10^{-41}\ \text{cgs}$$

and

$$\frac{3}{10}\pi^3\frac{\nu_{fi}^2}{c^2}\,|\psi_f^0|\, err\, |\psi_i^0\rangle|^2$$

$$\sim 6.8\times 10^{-43}\ \text{cgs}\ (\lambda = 5000\ \text{Å})$$

We thus see that the probability of magnetic dipole transition or electric quadrupole transition is negligibly small compared to the probability of electric dipole transition. The magnetic dipole transition is usually involved in magnetic resonance spectroscopy.

5.12 Line-Widths

One of the deficiencies of the time-dependent perturbation theory is that it leads to transitions that are infinitely sharp, although, in practice, spectral lines are broad and have finite line-widths. There are a number of causes for line broadening. In high resolution gas phase spectroscopy the Doppler effect causes line-widths. Pressure broadening is another phenomenon observed in gas phase spectroscopy. However, even if these contributions are eliminated there is a residual line-width, known as the natural line-width. The natural line-width is attributed to the fact that excited states of atoms and molecules have finite life times.

According to one form of Heisenberg's uncertainty principle,

$$\Delta E\times \Delta t \approx \hbar \left(\hbar = \frac{h}{2\pi}\right) \tag{5.117}$$

where ΔE is the uncertainty in energy and Δt is the duration of measurement of energy. If the atoms or molecules remain in their excited states for time τ, called the life time of the state, obviously, measurements of energy of that state cannot last longer than time τ. Thus the minimum uncertainty in this energy is

$$\Delta E \approx \frac{\hbar}{\tau} \tag{5.118}$$

Since the energy of a photon is $E = h\nu$, the error in the measurement of energy is $h\Delta\nu$ where $\Delta\nu$ is the error in the frequency. The spectral line is therefore fuzzed out over a frequency range $\Delta\nu$. This leads to the natural-width of the spectral lines.

This uncertainty in the energy was not accounted for in the time-dependent perturbation theory outlined in Sec. 5.7, since in obtaining Eq. (5.75) it was assumed that $\psi_f^{(0)}$ is an eigenvector of $\hat{H}_0$ with the energy $E_f^{(0)}$, independent of time. The ground state of an atom or a molecule in the absence of the radiation field has however infinite lifetime. So its energy is well defined by Eq. (5.118). The Eq. (5.75), however, allows for a build up of a final state $\psi_f^{(0)}$ by transition from a initial state $\psi_i^{(0)}$ but it does not account for the depletion of the state $\psi_f^{(0)}$ by transition from it. This probability can be allowed for by adding an extra term, i.e., $a_{ik}(t) \exp(-t/2\tau_k)$ to Eq. (5.75) for $\partial a_{if}(t)/\partial t$. Inclusion of this term then leads to finite line widths for transition.

5.13 Selection Rules

For many systems like atoms, molecules or harmonic oscillators, etc., the probability of a transition from a state given by $\psi_i^{(0)}$, to another state given by $\psi_f^{(0)}$, by light absorption or emission is proportional to $|r_{if}|^2$ [see Eq. (5.103)]. To determine whether such a transition in a given system is allowed or forbidden, the integral r_{if} defined as

$$r_{if} = e \int \psi_i^{(0)} \,|\, \hat{\mathbf{r}} \,|\, \psi_f^{(0)} \, dr$$

must be carefully examined. Instead of evaluating the transition dipole integral, simple symmetry arguments can be used to predict whether such integral vanishes or not, as in Sec. 3.6.

In the case of atoms this is simple. All atomic wavefunctions can be shown to be either symmetric or antisymmetric with respect to the operation of inversion of the electrons through the nucleus. Thus *s*, *d*, *g*, etc., orbitals ($l = 0, 2, 4, \ldots$) of the hydrogenic atoms are symmetric whereas *p*, *f*, *h*, etc., ($l = 1, 3, 5, \ldots$) are antisymmetric. In an atom whose wavefunction can be written as the product of one-electron orbitals, the state is symmetric if $\sum_i l_i$, i.e., the sum of the *l*-values of the occupied orbitals is an even number. The state becomes antisymmetric if $\sum_i l_i$ is an odd number. Now the operation of inversion on the operator $\hat{\mathbf{r}}$ ($\hat{\mathbf{r}} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$) always results in a change in the sign of $\hat{\mathbf{r}}$ as the coordinates x, y, z change to $-x, -y, -z$. Therefore the integral $\langle \psi_f^{(0)} \,|\, \hat{\mathbf{r}} \,|\, \psi_i^{(0)} \rangle$ be different from zero, if inversion on this integrand leaves its sign unchanged. Thus, the product $\psi_f^0 \cdot \psi_i^0$ must be antisymmetric with respect to inversion. This is possible if one of the two states is symmetric and the other antisymmetric. A hydrogen atom can therefore undergo dipole transitions of type $s \leftrightarrow p, p \leftrightarrow d, d \leftrightarrow f$. Apparently, a hydrogen atom in 2*s*-state cannot return to the ground 1*s*-state by dipole radiation. Thus, there exists a selection rule which states that in an electric dipole transition in the hydrogen or alkali atoms which have one electron in their outermost orbitals, the orbital angular momentum quantum number l must change by unity, or

$$\Delta l = \pm 1$$

This is the Laporte rule. According to this scheme transition $s \leftrightarrow s$, $p \leftrightarrow p$, etc., are forbidden. This means that transition between two states having the same orbital angular momenta is forbidden. This brings out a realisation that a photon which is emitted or absorbed during transition possesses an intrinsic angular momentum. This fact coupled with the law of conservation of angular mometum means that when a photon is emitted or absorbed by an atom angular momentum of the atom is decreased or increased. The restriction $\Delta l = \pm 1$ in such events implies that angular momentum projections of photon are limited to $\pm h/2\pi$ along the direction of propagation of the light. Unlike the electron which is a spin-$\frac{1}{2}$ particle, the photon is a spin-1 particle. The fact that a photon possesses an angular momentum also manifests in the existence of left and right-circularly polarised light.

Besides the electric dipole transitions, transitions through quadrupole and magnetic dipole radiations can occur. Selection rules for such transitions are different. According to Laporte rule, dipole transition is impossible between states having the same orbital angular momentum or i.e., $\Delta l = 0$. The electric quadrupole transition permits the selection rule $\Delta l = 0$ and $\Delta l = \pm 2$. This transition involves the operator $\widehat{\mathbf{rr}}$ (see Eq. 5.116) which is symmetric on inversion through the nucleus in an atom. Therefore, the integrand $\langle \psi_f^{(0)} \mid \widehat{\mathbf{rr}} \mid \psi_i^{(0)} \rangle$ remains unchanged in its sign if the product $\psi_f^{(0)} \cdot \psi_i^{(0)}$ is symmetric with respect to inversion. The magnetic dipole transition involves the operator $\hat{\mathbf{L}}$. The components of $\hat{\mathbf{L}}$, i.e., $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ behave like rotations about x, y, and z axes respectively. Therefore $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ are like axial vectors while the coordinates x, y, and z transform as ordinary polar vectors. The distinction between these two types of vectors is made in Fig. 5.5.

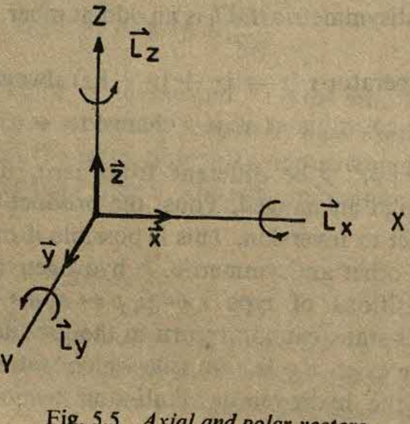

Fig. 5.5 *Axial and polar vectors*

Thus, while x, y, z become $-x$, $-y$, $-z$ on inversion through the origin or on reflections, $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ remain invariant on such operations. The selection rule for magnetic dipole transitions are therefore same, i.e., such transitions can occur between two states which are either both symmetric or both antisymmetric while the symmetric ↔ antisymmetric transition is forbidden. The violation of the Laporte rule can be caused by quadrupole or magnetic dipole transition. An example of such violation is found in the transition $s \leftrightarrow d$ of the O^{+2} and N^{+3} ions in the spectra of nebulae.

One may tend to think that the selection rule of the electric quadrupole transition is not compatible with the angular momentum of the photon that is emitted or absorbed. This transition occurs when the atom or molecule experiences a field gradient arising from the radiation. This imparts an additional angular momentum to the photon. The observed selection rules may then be derived if this extra source of angular momentum is taken into account.

In molecules, because of the nuclear motion we observe, rotational and vibrational spectra besides electronic spectra. Group theory proves to be a powerful tool for determining selection rules for various types of transitions in molecules. The student is referred to Herzberg's book[4,5] for detailed discussions.

PROBLEMS

1. Consider a trial wave function $\psi = Nx^a(1 - x^2)$ of an electron in one-dimensional box of unit length, where a is a parameter, and N, the normalising factor. Calculate its lowest energy by the variation method, assuming a hamiltonian of the form

$$\frac{h^2}{8\pi^2 m_e} \partial^2/\partial x^2$$

2. Employ a trial function $\psi(x) = \exp(-\alpha x^2)$ $(\alpha > 0)$ where α is a parameter. Calculate the zero-point energy of a harmonic oscillator whose hamiltonian is given by

$$\hat{H}(x) = -\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial x^2} + 2\pi^2\nu^2x^2$$

where the variable x extends over the range $(-\infty, \infty)$.

3. Find the effect of perturbation with an electric field ϵ, on a harmonic oscillator.
4. Calculate the spontaneous emission probability for a transition from a $2p$-to $1s$-orbital of atomic hydrogen.
5. In hydrogen atom a transition from $1s$ to $2s$ states is forbidden according to the Laporte rule. Show that, from perturbation theory, this selection rule breaks down if the hydrogen atom is placed in an external uniform electric field.
6. Using the principles of the time-independent perturbation theory outlined in Sec. 5.2, obtain the second-order correction to the wavefunction.
7. For the ground state of the hydrogen atom use the Gaussian trial function

$$\psi = \exp(-Cr^2)$$

Find the optimum value of C and the minimum energy.

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[4] G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, Princeton (1950).

[5] *Electronic spectra of polyatomic molecules*, Van Nostrand, Princeton (1967).

6

Many-Electron Atoms and Angular Momenta

6.1 The Wave Function of Many-Electron Systems

For atoms having many electrons, the electron repulsion terms must be included in the potential energy term of the wave equation. For example, the potential for an electron labelled 1 will be given by (in atomic units)

$$V = -\frac{Z}{r_1} + \sum_{j\neq 1} \frac{1}{r_{1j}} \tag{6.1}$$

where r_1 is the distance of the electron labelled '1' from the atomic nucleus of charge Z, and r_{1j}, the interelectronic distance between electron '1' and electron j. Every other electron will be subjected to a similar potential field in an atom and therefore, the potential energy of system of many electrons in an atom of atomic number Z will be given by

$$V = -\sum_i \frac{Z}{r_i} + \frac{1}{2} \sum_{i\neq j} \frac{1}{r_{ij}} \tag{6.2}$$

where the factor $\frac{1}{2}$ in the second term is introduced to avoid each 'r_{ij}' term being counted twice in the summation. The hamiltonian of such a system is then

$$\hat{H} = -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_i Z/r_i + \tfrac{1}{2}\sum_{i\neq j} \frac{1}{r_{ij}} \tag{6.3}$$

where ∇_i is as before, the laplacian (or the kinetic energy operator) for the electron i. In Eq. (6.3) the first two terms are the one-electron terms and the third term, a sum of two-electron terms. Owing to the presence of these two-electron terms in $\hat{H}$ it is not possible to separate the variables as it was possible in the treatment of hydrogen-like atoms. As a starting point we assume that electrons are independent of each other so that the approximate hamiltonian is given by

$$\hat{H}' = \sum_i \hat{H}_i = -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_i V_i \tag{6.4}$$

where V_i is an effective one-electron potential of electron 'i'.

If $\phi_1(1), \phi_2(2) \ldots \phi_n(n)$ are the one-electron orbitals of electrons labelled $1, 2, \ldots n$ respectively then one can write the following wave equations for each electron

$$\begin{aligned}\hat{H}_1\phi_1(1) &= E_1\phi_1(1)\\ \hat{H}_2\phi_2(2) &= E_2\phi_2(2)\\ \cdots\cdots &\quad \cdots\cdots\\ \cdots\cdots &\quad \cdots\cdots\\ \hat{H}_n\phi_n(n) &= E_n\phi_n(n)\end{aligned} \tag{6.5}$$

where $\hat{H}_i = -\frac{1}{2}\nabla_i^2 - V_i$ and E_i is the eigenvalue of $\hat{H}_i$. These one-electron functions, i.e. $\phi_1, \phi_2 \ldots \phi_n$, can be combined together in some way to generate an overall wave function for the atom. This "one-electron approximation" is, in fact, used as the first approximation to the true solution. The exact solution of a many-electron system is not obtained. This is not a limitation of quantum mechanics alone; the many-body problem has not been solved classically either.

If we assume the total wave function of a n-electron system as the simple product of n one-electron functions, as

$$\Psi(1, 2, 3, \ldots n) = \phi_1(1)\phi_2(2)\phi_3(3) \ldots \phi_n(n) \tag{6.6}$$

then

$$\begin{aligned}\hat{H}\Psi &= (\hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \ldots \hat{H}_n)[\phi_1(1)\phi_2(2) \ldots \phi_n(n)]\\ &= \hat{H}_1\phi_1(1)\cdot\phi_2(2)\phi_3(3) \ldots \phi_n(n)\\ &\quad + \hat{H}_2\phi_2(2)\cdot\phi_1(1)\phi_3(3)\phi_4(4) \ldots \phi_n(n) + \ldots\\ &\quad H_n\phi_n(n)\cdot\phi_1(1)\phi_2(2)\phi_3(3) \ldots \phi_{n-1}(n-1)\\ &= [(E_1 + E_2 + E_3 + \ldots E_n)][\phi_1(1)\phi_2(2)\phi_3(3) \ldots \phi_n(n)]\\ &= (E_1 + E_2 + E_3 + \ldots E_n)\Psi\end{aligned} \tag{6.7}$$

On the other hand, if we assume that the possible overall function be given by

$$\Psi(1, 2, 3 \ldots n) = \phi_1(1) + \phi_2(2) + \phi_3(3) + \ldots \phi_n(n) \tag{6.8}$$

then we have

$$\begin{aligned}\hat{H}\Psi &= E_1\phi_1(1) + E_2\phi_2(2) + \ldots E_n\phi_n(n)\\ &\neq (E_1 + E_2 + E_3 \ldots . E_n)\cdot\Psi\end{aligned} \tag{6.9}$$

This suggests that only the product wave function of the form (6.6) gives equations of the right form. Thus, total wave function of a many-electron system is given approximately by a product of one-electron functions while their total energy is the sum of the one-electron energies of all electrons.

In a previous chapter we have seen that there are two different spin states for each electron ($\lambda = \pm\frac{1}{2}$). We shall represent the spin wave functions for these two states by α and β corresponding to $\lambda = +\frac{1}{2}$ and $\lambda = -\frac{1}{2}$ respectively. The combined space and spin function of an electron is called a spin-orbital. Let us write the overall wave function of a many-electron system as

$$\phi_1(1)\phi_2(2)\phi_3(3)\ldots\phi_n(n) \tag{6.10}$$

in which ϕ_1 is a spin-orbital which accommodates the electron 1, ϕ_2 the electron 2, etc. But electrons are indistinguishable particles. So an equally good overall wave function would be

$$\phi_1(2)\phi_2(1)\phi_3(3)\ldots\phi_n(n) \tag{6.11}$$

or any other similar product. In fact, one can write the $n!$ number of such product functions which can be obtained by permuting the n electrons amongst the n spin-orbitals. Since the product functions of the form (6.10) and (6.11) should occur with equal probability as there is no way to distinguish one from the other, the most general overall wave function will be a linear combination of these $n!$ functions which occur with equal weight.

Pauli put forth a fundamental principle which states that the overall wave function of a system must be antisymmetric with respect to interchange of every pair of electrons. This means that a particular linear combination of the $n!$ functions, which changes sign on exchanging the coordinates of any two electrons is permissible. For a system of two electrons, a wave function of the form

$$\psi = \phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1) \tag{6.12a}$$

changes sign on interchanging the positions of the electron pair in the orbitals ϕ_1 and ϕ_2. Thus

$$\psi' = \phi_1(2)\phi_2(1) - \phi_1(1)\phi_2(2) = -\psi \tag{6.12b}$$

For a system of many electrons this can be achieved by the use of a determinant and by allocating one electron to each row or column. Thus, the overall wave function of a n-electron system is written as

$$\Psi(1, 2, 3, \ldots n) = \begin{vmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_n(2) \\ \phi_1(3) & \phi_2(3) & \ldots & \phi_n(3) \\ \phi_1(n) & \phi_2(n) & \ldots & \phi_n(n) \end{vmatrix} \tag{6.13}$$

In Eq. (6.13) the exchange of any two electron coordinates is equivalent to exchanging two rows of the determinant and according to the property of determinants, this changes the sign of the function. The abbreviated way of writing a determinantal wave function of the form (6.13) is

$$\Psi(1, 2, 3, \ldots n) = \sum_P (-1)^\nu P\phi_1(1)\phi_2(2)\ldots\phi_n(n) \tag{6.14}$$

where P is an operator which permutes the variables 1, 2, 3 . . . n among themselves and ν is called parity, which is equal to the number of interchanges involved in a particular permutation.

The wave function (6.13) or (6.14) must be normalised, i.e.

$$\int \Psi^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \ldots d\tau n = 1 \tag{6.15}$$

The square of Ψ contains large number of terms

$$\left(\text{i.e. } n! + \frac{n!(n! - 1)}{2}\right)$$

of which $n!$ being the number of individual terms squared, i.e. $[\phi_1(1)\phi_2(2) \ldots \phi_n(n)]^2$, etc. and the rest being the cross product of the form $2\times [\phi_1(1)\phi_2(2) \ldots \phi_n(n) \times \phi_1(2)\phi_2(1) \ldots \phi_n(n)]$, etc. It is necessary to evaluate the $n!$ number of integrals of the form

$$\int [\phi_1(1)\phi_2(2)\phi_3(3) \ldots \phi_n(n)]^2 \, d\tau_1 \, d\tau_2 \ldots d\tau_n$$

$$= \int \phi_1^2(1) \, d\tau_1 \int \phi_2^2(2) \, d\tau_2 \int \phi_3^2(3) \, d\tau_3 \ldots \int \phi_n^2(n) \, d\tau_n = 1 \tag{6.16}$$

since the orbitals ϕ_1, ϕ_2, etc. are normalised. The integrals of the form arising from the cross product in Eq. (6.15) are

$$\int \phi_1(1)\phi_2(2) \ldots \phi_n(n) \int \phi_1(2)\phi_2(1) \ldots \phi_n(n) d\tau_1 \, d\tau_2 \, d\tau_3$$

$$= \int \phi_1(1)\phi_2(1) \, d\tau_1 \int \phi_2(2)\phi_1(2) \, d\tau_2 \int \phi_3(3)\phi_3(3) \, d\tau_3 \ldots$$

$$\int \phi_n(n)\phi_n(n) \, d\tau_n = 0 \tag{6.17}$$

since $\phi_1, \phi_2 \ldots$ are mutually orthogonal. Since there are altogether $n!$ number of integrals of the form (6.16) we have

$$\int \Psi^2 \, d\tau_1 \, d\tau_2 \ldots d\tau_n = n! \tag{6.18}$$

The normalised wave function of a n-electron system is then written as

$$\Psi(1, 2, 3 \ldots n) = \frac{1}{\sqrt{n!}} \sum_P (-1)^\nu P\phi_1(1)\phi_2(2) \ldots \phi_n(n) \tag{6.19}$$

The conventional way of writing a determinantal wavefunction is to write down only the diagonal terms which in the above case are

$$\frac{1}{\sqrt{n!}} \mid \phi_1(1)\phi_2(2)\phi_3(3) \ldots \phi_n(n) \mid \tag{6.20}$$

The determinantal form of the wavefunction of a many-electron system is referred to as Slater determinant.

Often the elements of the determinant are abbreviated further by using the fact that each orbital in an atom or a molecule can accommodate two electrons, one with α-spin, and the other with β-spin. Therefore, one can write the overall wave function of a n-electron system (suppose, n is an even number) as

$$\frac{1}{\sqrt{n!}}\left|\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\ \ldots\ \bar{\varphi}_{n/2}(n)\right| \tag{6.21}$$

where $\varphi_1\varphi_2 \ldots \varphi_{n/2}$ etc. are the space part of the orbitals such that $\varphi_1(1)$ denotes the electron '1' occupying the orbital φ_1 with α-spin and $\overline{\varphi_1}(2)$, the electron '2' in the orbital φ_1 with β-spin. If we attempt to build up a wave function in which any two electrons occupy the same orbital with same spin function then two rows in the determinant (6.21) are identical. But a determinant with two identical rows vanishes and therefore such a wave function becomes trivial.

6.2 The Helium Atom

The helium atom has two electrons moving in a field of a nucleus of charge $+2e$. In this atom, besides an attractive interaction between electrons and nucleus there is a repulsive interaction between the two electrons. The hamiltonian operator of the helium atom (in atomic units) can then be written as

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \tag{6.22}$$

where electrons are lebelled 1 and 2 and the coordinates are defined as shown in Fig. 6.1.

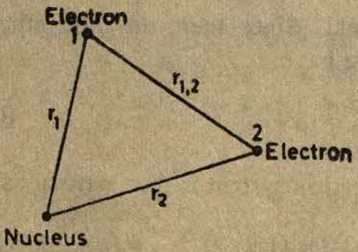

Fig. 6.1 *The coordinate system for the helium atom*

For the ground state of helium the electronic configuration is $1s^2$. The overall wave function will be given by a Slater determinant:

$$\Psi_0 = \frac{1}{\sqrt{2}}\ |\ 1s(1)\ \overline{1s}(2)\ |^{*} \tag{6.23}$$

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*"1s" stands for the wave function of the "1s" spin-orbital in the helium atom.

which on expansion may be written as

$$\Psi_0 = \frac{1}{\sqrt{2}}\ 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{6.24}$$

According to the variation method the energy, ϵ, based on approximate wave function of the form (6.23) is always higher than true energy, E_0 of the ground state. We shall now evaluate ϵ.

$$\begin{aligned} \epsilon &= \langle \Psi_0 \mid H \mid \Psi_0 \rangle \\ &= \tfrac{1}{2}\langle 1s(1)1s(2) \mid H \mid 1s(1)1s(2) \rangle \\ &\quad \times \langle (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \mid (\alpha(1)\beta(2) - \beta(1)\alpha(2) \rangle \end{aligned} \tag{6.25}$$

The second integral in Eq. (6.25) is over spin space. Since the spin functions α and β are individually normalised and mutually orthogonal, one can easily show that

$$\begin{aligned} &\langle (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \mid [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \rangle \\ &= \int \alpha^2(1)\ ds_1 \int \beta^2(2)\ ds_2 + \int \beta^2(1)\ ds_1 \int \alpha^2(2)\ ds_2 \\ &\qquad -2 \int \alpha(1)\beta(1)\, ds_1 \int \alpha(2)\beta(2)\ ds_2 \\ &= 2 \end{aligned} \tag{6.26}$$

Thus

$$\epsilon = \langle 1s(1)\ 1s(2) \mid H \mid 1s(1)\ 1s(2) \rangle \tag{6.27}$$

If we write the hamiltonian (6.22) more compactly as

$$H = H_1 + H_2 + \frac{1}{r_{12}} \tag{6.28}$$

where

$$H_i = -\tfrac{1}{2}\nabla_i^2 - 2/r_i \tag{6.29}$$

then the energy is

$$\begin{aligned} \epsilon &= \langle 1s(1)1s(2) \mid \left(H_1 + H_2 + \frac{1}{r_{12}}\right) \mid 1s(1)1s(2) \rangle \\ &= \langle 1s(1) \mid H_1 \mid 1s(1) \rangle \langle 1_s(2) \mid 1s(2) \rangle + \langle 1s(2) \mid H_2 \mid 1s(2) \rangle \\ &\quad \times \langle 1s(1) \mid 1s(1) \rangle + \langle 1s(1)1s(2) \left|\frac{1}{r_{12}}\right| 1s(1)\ 1s(2) \rangle \end{aligned} \tag{6.30}$$

$$= E_{1s}(1) + E_{1s}(2) + J \tag{6.31}$$

where $E_{1s}(i)$ is the energy of i^{th} electron in the $1s$ orbital of helium and J, called the coulomb integral, is defined by the last term in Eq. (6.30) and it measures the coulombic repulsion between electrons.

We shall now give more explicit expression for $E_{1s}(i)$. When an electron, say '1' is quite far from the nucleus of charge +2 and the electron '2' is close to the nucleus, the potential acting on electron '1' is $-(2-1)/r_1$ because the electron '2' can virtually screen the nucleus.

When the electron '1' comes very close to the nucleus while the electron '2' goes farther out from the nucleus, the potential acting on the electron '1' is then $-2/r_1$. One expects that the average potential acting on an electron must vary between these two extremes. Let us assume Z', the effective nuclear charge experienced by an electron in the helium atom where Z' will have value somewhere between 1 and 2. The best value of Z' will be determined by the variation principle. The wave function of $1s$-orbital appropriate to this effective nuclear charge Z' is

$$1s = \left[\frac{Z'^3}{\pi}\right]^{1/2} \exp(-Z'r) \tag{6.32}$$

This orbital wave function is an eigenfunction of

$$-\tfrac{1}{2}\nabla^2 - Z'/r$$

with eigenvalue $-Z'^2/2$ (see Sec. 4.14). We obtain for $E_{1s}(i)$

$$\begin{aligned} E_{1s}(i) &= \langle 1s(i) \mid -\tfrac{1}{2}\nabla_i^2 - \frac{2}{r_i} \mid 1s(i) \rangle \\ &= \left\langle 1s(i) \left| -\tfrac{1}{2}\nabla_i^2 - \frac{Z'}{r_i} \right| 1s(i) \right\rangle - \left\langle 1s(i) \left| \frac{2-Z'}{r_i} \right| 1s(i) \right\rangle \\ &= -\frac{Z'^2}{2} \langle 1s(i) \mid 1s(i) \rangle - (2-Z') \left\langle 1s(i) \left| \frac{1}{r_i} \right| 1s(i) \right\rangle \\ &= -\frac{Z'^2}{2} - (2-Z') \left\langle 1s(i) \left| \frac{1}{r_i} \right| 1s(i) \right\rangle \end{aligned} \tag{6.33}$$

Since electrons '1' and '2' are equivalent, $E_{1s}(1)$ and $E_{1s}(2)$ are equal. Therefore Eq. (6.31) may be rewritten as

$$\epsilon = -Z'^2 - 2(2-Z') \left\langle 1s(1) \left| \frac{1}{r_1} \right| 1s(1) \right\rangle + J \tag{6.34}$$

The evaluation of the integral $\left\langle 1s(1) \left| \frac{1}{r_1} \right| 1s(1) \right\rangle$ is very simple and is as follows:

$$\begin{aligned} \left\langle 1s(1) \left| \frac{1}{r_1} \right| 1s(1) \right\rangle &= \frac{Z'^3}{\pi} \int_0^\infty \frac{\exp(-2Z'r_1)}{r_1} r_1^2\, dr_1 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \\ &= \frac{Z'^3}{\pi} \cdot 4\pi \int_0^\infty \exp(-2Z'r_1) r_1 dr_1 \end{aligned}$$

[see Eq. (5.57) for evaluation of this integral]

$$= \frac{4Z'^3}{4Z'^2} = Z' \tag{6.35}$$

It, however, remains to evaluate the two-electron integral J which gives the mutual repulsion energy of the two electrons. It is shown in the Appendix 6 [Eq. (A6.7)] that J has the value $(5/8)Z'$.

The result of calculation then leads to

$$\epsilon = -Z'^2 - 2(2-Z')Z' + \frac{5}{8}Z' = Z'^2 - \frac{27}{8}Z' \tag{6.36}$$

The value of Z' which minimises the energy is found by differentiating ϵ with respect to Z'.

Setting $\frac{\partial \epsilon}{\partial Z'} = 0$, one obtains

$$2Z' - 27/8 = 0$$

or

$$Z' = 27/16 = 1.69 \tag{6.37}$$

Substitution of this value for Z' into Eq. (6.36) gives the approximate ground state energy of the helium atom as

$$\begin{aligned}\epsilon &= -2.8476 \text{ (a.u.)}\\ &= -77.48 \text{ eV}\end{aligned} \tag{6.38}$$

The experimental value is -2.904 a.u. (79.00 eV). Thus this simple calculation accounts for 98% of the observed energy. To an electron the effective nuclear charge appears to have the value of 1.69 instead of the true charge of 2. The quantity 0.31 represents the screening of the nucleus by the other electron.

6.3 Many-Electron Atom

The electronic structure of many-electron atoms can be qualitatively understood in terms of hydrogen-like orbitals. According to Pauli's exclusion principle, each such orbital can accommodate two electrons with opposed spins. Using this principle, electrons are fed into each orbital starting with the one of lowest energy and continuing in the order of increasing energy. This method of building up the atomic structure is known as the 'Aufbau' principle.

We have found in a previous chapter that an electron in a state of high angular momentum tends to stay farther from the nucleus than an electron in a state of low angular momentum. Thus, in a poly-electronic atom as l increases, the orbital penetrates less into the region close to the nucleus (Fig. 6.2).

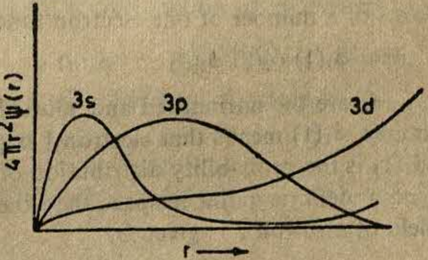

Fig. 6.2 *Probability density as a function of distance from the nucleus*

The average nuclear charge experienced by an electron belonging to an orbital of the large l value should decrease as the nuclear charge is screened by other electrons having lower l. Let σ, called the screening constant, determine the extent to which the nuclear charge is screened by electrons having lower angular momentum in an atom. The effective nuclear charge experienced by an electron in an orbital with larger angular momentum is then $Z-\sigma$, and the energy of that electron is approximately given by (Chapter 4).

$$E = -\frac{2\pi^2 m_e (Z - \sigma)^2 e^4}{n^2 h^2} \tag{6.39}$$

Since σ is positive and increases with l, the energy increases with l. The conventional values of σ for the orbitals with principal quantum number equal to 1, 2, or 3 are given by the approximate Slater's rules based on application of the variation theorem. The rules are as follows:

1. The orbitals are divided into the following groups:

   $1s$, $2s$, $2p$; $3s$, $3p$; $3d$; etc.

2. σ is calculated as the sum of the following contributions:
   (a) Nothing from any orbital higher than the one considered.
   (b) An amount of 0.35 for every other electron in the group (except for the $1s$-group where 0.30 is taken).
   (c) If the orbital considered is an s or p shell an amount of 0.85 from each electron with principal quantum number less by 1 and an amount of 1.00 from each electron still further in.

For example, nitrogen atom has two $1s$-electrons, two $2s$-electrons and three $2p$-electrons. For the $1s$-orbital $\sigma = 0.30$, for the $2s$ and $2p$ orbitals $\sigma = 4\times0.35 + 2\times0.85 = 3.10$.

6.4 Hartree and Hartree-Fock Self-Consistent Field Methods

These are the powerful methods for the calculation of the ground state energy and wave functions of many-electron atoms or ions. In an earlier work of Hartree, the wave function of an atom containing n electrons was written as the product of n number of one-electron functions, as

$$\psi = \phi_1(1)\,\phi_2(2)\,\phi_3(3)\,\ldots\,\phi_n(n) \tag{6.40}$$

where $\phi_1, \phi_2, \phi_3, \ldots \phi_n$ are the normalised and mutually orthogonal one-electron wave functions. $\phi_1(1)$ means that electron 1 is put in the orbital ϕ_1 etc. The quantity $\phi_1^2(1)$ is the probability distribution of electron 1. If electron 1 is placed at a definite point in space then the potential energy of electron 1 in the field of electron 2 is given by

$$V_1 = \int \phi_2^2(2)/r_{12}\cdot d\tau_2 \tag{6.41}$$

where r_{12} is the distance between electrons 1 and 2 and the integral in Eq. (6.41) is over the entire space accessible to electron 2. Similar contributions to the potential energy of electron 1 are made by every other electron in atom. In general, the total potential energy of electron 1 can be written as [see Eq. (6.2)].

$$V_1 = -\frac{Z}{r_1} + \sum_{i \neq 1} \int \frac{\phi_i^2(i)}{r_{1i}}\, d\tau_i \tag{6.42}$$

A similar expression can be written down for every other electron in the atom. Thus

$$V_i = -\frac{Z}{r_i} + \sum_{j \neq i} \int \frac{\phi_j^2(j)}{r_{ij}}\, d\tau_j \tag{6.43}$$

Wave function of an electron moving in a potential field given by Eq. (6.43) is obtained from the solution of the Schrödinger equation

$$(-\tfrac{1}{2}\nabla_i^2 + V_i)\, \phi_i(i) = \epsilon_i \phi_i(i) \tag{6.44}$$

where ϵ_i is the energy of the i^{th} orbital, ϕ_i which is assumed normalised. Since there are n number of such orbitals, there are n such simultaneous equations of the form (6.44).

These non-linear simultaneous equations cannot be solved because V_i requires the prior knowledge of all other one-electron wavefunctions ϕ_j, etc. [Eq. (6.43)]. However, Hartree suggested the following method.

First, an arbitrary set of ϕ_j, ϕ_l . . . etc. are chosen. These may be the appropriate Slater orbitals. The field arising from all electrons except the i^{th} electron is calculated from the chosen set of functions and ϕ_i is then calculated from Eq. (6.44) by a numerical method. This procedure is carried on for each of n-electrons in the atom. The calculated set of ϕ_i will not, in general, be identical with the original set assumed. The calculations are now repeated using the calculated set of functions instead of Slater orbitals as used earlier. This process of iteration is to be continued until the assumed set of ϕ_i and the calculated set are identical at which point the solution of the set of simultaneous equations is said to have been achieved. This method of solution is also called the self-consistent field method.

Let $\phi_1'(1)$. $\phi_2'(2)$ . . . be the self-consistent field one-electron wave functions. Then, the total wave function of an n-electron system is given as

$$\Psi'(1, 2, 3, \ldots n) = \phi_1'(1)\phi_2'(2) \ldots \phi_n'(n) \tag{6.45}$$

The energy ϵ associated with this wave function is

$$\begin{aligned}
\epsilon &= \langle \Psi' \mid H \mid \Psi' \rangle \\
&= \Big\langle \phi_1'(1)\phi_2'(2) \ldots \phi_n'(n) \Big| -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} \\
&\quad + \frac{1}{2}\sum_{i \neq j} \frac{1}{r_{ij}} \Big| \phi_1'(1)\phi_2'(2) \ldots \phi_n'(n) \Big\rangle \\
&= \sum_i \Big\langle \phi_i'(i) \Big| -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \Big| \phi_i'(i) \Big\rangle \\
&\quad + \frac{1}{2}\sum_{\substack{i \\ i \neq j}} \sum_{j} \Big\langle \phi'(i)\phi_j'(j) \Big| \frac{1}{r_{ij}} \Big| \phi_i'(i)\phi_j'(j) \Big\rangle
\end{aligned} \tag{6.46}$$

If we multiply the self-consistent field form of Eq. (6.44) with $\phi'_i(i)$ and integrate, we have

$$\epsilon'_i = \left\langle \phi'_i(i) \left| -\frac{1}{2}\nabla_i^2 + V_i \right| \phi'_i(i) \right\rangle$$

$$= \left\langle \phi'_i(i) \left| -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right| \phi'_i(i) \right\rangle$$

$$+ \sum_{j \neq i} \left\langle \phi'_i(i)\phi'_j(j) \left| \frac{1}{r_{ij}} \right| \phi'_i(i)\phi'_j(j) \right\rangle \tag{6.47}$$

where ϵ'_i is the self-consistent field energy of the orbital, $\phi'_i(i)$. Then, Eq. (6.46) can be written as

$$\epsilon = \sum_i \epsilon'_i - \frac{1}{2} \sum_i \sum_{\substack{j \\ i \neq j}} \left\langle \phi'_i(i)\phi'_j(j) \left| \frac{1}{r_{ij}} \right| \phi'_i(i)\phi'_j(j) \right\rangle \tag{6.48}$$

because, ϵ'_i involves, in addition to its own orbital energy in the field of the nucleus, the interaction with all other electrons in atoms so that in the summation $\sum_i \epsilon'_i$ the interaction between electrons are counted twice. This additional interaction energy is therefore subtracted from $\sum_i \epsilon'_i$ to obtain the correct energy. If an electron labelled k from the orbital ϕ_k is removed to infinity, the atom becomes ionised. If we ignore any change of the orbital functions the energy of the ion is then given by

$$\epsilon_{ion} = \sum_{i \neq k} \epsilon'_i - \frac{1}{2} \sum_{i \neq k} \sum_{\substack{j \neq k \\ i \neq j}} \left\langle \phi'_i(i)\phi'_j(j) \left| \frac{1}{r_{ij}} \right| \phi'_i(i)\phi'_j(j) \right\rangle$$

$$= \epsilon - \left[\left\langle \phi'_k(k) \left| -\frac{1}{2}\nabla_k^2 - \frac{Z}{r_k} \right| \phi'_k(k) \right\rangle \right.$$

$$\left. + \sum_{j \neq k} \left\langle \phi'_k(k)\phi'_j(j) \left| \frac{1}{r_{jk}} \right| \phi'_k(k)\phi'_j\cdot(j) \right\rangle \right] \tag{6.49}$$

Thus we have the relation

$$-\epsilon'_k = \epsilon_{ion} - \epsilon \tag{6.50}$$

This means that $-\epsilon'_k$ represents the ionisation energy of the atom in which an electron is removed from the orbital, ϕ_k. This method has been applied by Hartree to several atoms and ions.

The Hartree's wave function of the form given by Eq. (6.40), however, does not satisfy the antisymmetry requirement. Fock has shown later that this method can be modified taking into account the electronic exchange between the orbitals and thereby satisfying the antisymmetry requirement. This method is called the Hartree-Fock self-consistent field method which employs the Slater determinantal form of wave function

$$\Psi(1, 2, 3 \ldots n) = \frac{1}{\sqrt{n!}} \left| \phi_1(1)\phi_2(2) \ldots \phi_n(n) \right| \tag{6.51}$$

where $\phi_1, \phi_2, \ldots \phi_n$ are the spin orbitals which are mutually orthogonal. By proceeding as above, one obtains a set of equations which are similar in form to the Hartree equation (6.44), except that V_i now contains additional terms corresponding to the potential energy arising from the electron interchange. The results for atoms and ions do not differ much from those obtained by the Hartree method. The atomic orbitals that are obtained by the Hartree-Fock self-consistent field procedure are either given as a table of numbers or they may be expressed algebraically in the form

$$\phi = [\sum_{n,\zeta} C(n, \zeta)\chi(n, \zeta)]Y_{l,m}(\theta, \phi) \tag{6.52}$$

where

$$\chi(\zeta, n) = \exp(-\zeta r)r^n \tag{6.53}$$

and $C(n, \zeta)$ are the coefficients of $\chi(n, \zeta)$, $Y_{l,m}(\theta, \phi)$ is the spherical harmonic, defined already in a previous Chapter. Since the angular momentum operators commute with the atomic hamiltonian (this will be shown later in this Chapter), atomic orbital wave functions written in the form (6.52) have the spherical harmonic as a factor of wave function. The principal quantum number n has no longer any significance as we do not obtain any simple algebraic formula for energy in which n appears as an integer. It should be obvious now, how approximate is the Slater atomic orbital which corresponds to only one term in the summation of Eq. (6.52). A table of Hartree-Fock self-consistent field atomic functions for various atoms and ions has been prepared by Clementi.[1]

6.5 Electron Correlation in the Helium Atom

It has been shown in Sec. 6.2 that the energy of a helium atom obtained using a 1s orbital with screened nuclear charge is different from the true energy by 0.52 eV. However, this screened hydrogen-like function is not the best 1s-orbital which can be obtained by the Hartree-Fock self-consistent field procedure. The best energy obtained using this procedure is -77.866 eV which is still 0.134 eV above the observed energy.

There are several factors which can contribute to this difference. The most dominant of all is the error in the single-configuration wave function of the form (6.23) which describes that the position of the two electrons is independent of each other. But, in view of the mutual repulsion, the electrons have a tendency to avoid each other. This tendency of electrons is known as electron correlation. Any wave function which satisfies the Pauli exclusion principle takes into account the spin correlation. When the repulsion of electrons arises from their electrostatic charges, it is referred to as charge-correlation.

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[1] E. Clementi, *Tables of Atomic Functions*, IBM Corporation San Jose, California, U.S.A., 1965.

There is no straight forward procedure to make the correction for charge correlation in a wave function. In 1929 Hylleraas studied the ground state of the helium atom. He multiplied the uncorrelated wave function,

$$\exp\,[-Z'(r_1 + r_2)]$$

with a polynomial in r_1, r_2 and r_{12}. Thus the wave function has the form

$$\exp\,[-Z'(r_1 + r_2)]\{1 + f(r_1, r_2, r_{12})\} \tag{6.54}$$

Hylleraas used a polynomial which contained fourteen terms. Each term involved an adjustable constant and these as well as Z' were adjusted to minimise the energy. The calculated energy was very close to the observed one. But this method is very complicated and the extension of this method beyond two-electron problems is quite hopeless.

Another procedure to make correction for the charge-correlation is to retain the Slater determinant using hydrogen-like wave functions and to consider the possible interactions between the appropriate electronically excited states of right symmetry. This approach is known as the configuration-interaction and was employed by Taylor and Parr.[2] Since every atom is associated with the spherical charge distribution around its nucleus Taylor and Parr pointed out that there were two types of charge correlation.

(1) Radial correlation; One electron tends to be close to the nucleus and the other near the surface of the sphere.
(2) Angular correlation; Two electrons tend to be at the opposite ends of the diameter of the sphere.

Taylor and Parr suggested that the correction for the radial correlation could be achieved by adding to the $1s^2$ function [Eq. (6.23)], a contribution from a $1s'2s'$ function because a $2s$ function favours the electron being further from the nucleus. Thus, they had the following approximate wave function for the helium atom:

$$\Psi = a_1 1s^{z'}(1)1s^{z'}(2) + a_2[1s^{z'}(1)2s^{z'}(2) + 1s^{z'}(2)2s^{z'}(1)] \tag{6.55}$$

where $1s^{z'}$ and $2s^{z'}$ refer to the $1s$- and $2s$-orbitals with z' being the orbital exponent, the form of the last pair of terms is required by the symmetry of the system. The constants, z', a_1 and a_2 were chosen to minimise the energy. Their result showed a slight improvement in energy. Taylor and Parr added further configurations involving other spherically symmetric functions such as $(1s, 3s)$, $(2s, 2s)$, $(2s, 3s)$ and $(3s, 3s)$ etc. and obtained a reliable estimate of the radial correlation energy which was defined as the difference between the Hartree-Fock energy and the energy calculated using the best superposition of all configurations obtainable from a complete set of purely radial one-electron functions (e.g. all ns hydrogen-like functions).

Then, Taylor and Parr allowed for the angular correlation by superposing the configurations built from the angularly dependent orbitals. They added the configurations like $2p^2$, $3d^2$ and $4f^2$ and obtained a better improvement in energy than in dealing with the radial correlation. Then they combined the two sets of configurations to allow for both the radial and angular correlation and obtained energy within 0.2% of the observed value. Their final conclusion was that for the ground state of the helium atom, the angular correlation was more important than the radial one.

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[2] G.R. Taylor and R.G. Parr, *Proc. Natn. Acad. Sci.*, (U.S.A.), **38**, 154, 1952.

6.6 Angular Momenta Introduction

In Chapter 2, we have already given the classical definition of angular momentum and also shown how the various components of the orbital angular momentum and the total orbital angular momentum are represented by the quantum mechanical operators. The purpose of this and the following sections is to discuss in greater detail the various properties of three types of angular momentum, viz. orbital angular momentum, spin angular momentum and the total angular momentum resulting from a vector coupling of orbital and spin angular momenta, because they are very useful for the classification and description of atomic states.

If L_x, L_y and L_z be the three components of the orbital angular momentum, then

$$L^2 = L \cdot L = L_x^2 + L_y^2 + L_z^2$$

L^2 is called the total orbital angular momentum squared. In Sec. 3.9 it was shown that wave functions of a rigid rotator were also the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$. The eigenvalue equations in atomic units are

$$\hat{L}^2 Y_{l,m} = l(l+1) Y_{l,m}$$

$$\hat{L}_z Y_{l,m} = m Y_{l,m} \tag{6.56}$$

where the functions $Y_{l,m}$ are the spherical harmonics. The quantum number l can have the values 0, 1, 2, 3, . . . and for a given value of l, m can nave $2l + 1$ values, i.e., $l, l - 1, l - 2 \ldots 0 \ldots -(l - 1), -l$. In Chapter 4 we saw that the functions $Y_{l,m}$ described the angular variation of atomic orbitals. Therefore, we identify the integers l and m, respectively, with the quantum numbers determining the total orbital angular momentum and a component of this momentum in an arbitrary direction.

6.7 Commutation Relations

Many of the properties of angular momentum operators are derived from their commutation relations. The commutator of $\hat{L}_x$ and $\hat{L}_y$ is obtained as follows. Using the definitions of $\hat{L}_x$ and $\hat{L}_y$ [Eq. (2.46)] and employing the atomic units one obtains

$$\hat{L}_x \hat{L}_y = \frac{1}{i}\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \cdot \frac{1}{i}\left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}\right)$$

$$= -\left[y\frac{\partial}{\partial z}\cdot z\frac{\partial}{\partial x} - y\frac{\partial}{\partial z}\,x\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\,z\frac{\partial}{\partial x} + z\frac{\partial}{\partial y}\,x\frac{\partial}{\partial z}\right]$$

$$= -\left[y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - yx\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + zx\frac{\partial^2}{\partial y\partial z}\right] \tag{6.57}$$

$$\hat{L}_y\hat{L}_x = -\left[z\frac{\partial}{\partial x}\,y\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\,z\frac{\partial}{\partial y} - x\frac{\partial}{\partial z}\,y\frac{\partial}{\partial z} + x\frac{\partial}{\partial z}\,z\frac{\partial}{\partial y}\right]$$

$$= -\left[zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial z\partial y} - x\frac{\partial}{\partial y}\right] \tag{6.58}$$

Subtracting Eq. (6.58) from Eq. (6.57)

$$[L_x, L_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = -\left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right]$$

$$= \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = i\hat{L}_z \tag{6.59}$$

Thus, the operators $\hat{L}_x$ and $\hat{L}_y$ do not commute. Similarly, one finds

$$[L_y, L_z] = \hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y = i\hat{L}_x \tag{6.60}$$

$$[L_z, L_x] = \hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z = i\hat{L}_y \tag{6.61}$$

It is, however, important to note that the components of linear momenta commute with each other, i.e.

$$[P_x, P_y] = [P_y, P_z] = [P_z, P_x] = 0 \tag{6.62}$$

In this respect angular momentum is fundamentally different from the linear momentum whose three components can simultaneously have definite values.

We shall now consider the commutation relations between $\hat{L}^2$ and its components.

$$[L_x^2, L_z] = \hat{L}_x^2\hat{L}_z - \hat{L}_z\hat{L}_x^2$$

$$= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_x$$

$$= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_x\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z\hat{L}_x - \hat{L}_z\hat{L}_x\hat{L}_x$$

$$= \hat{L}_x[L_x, L_z] + [L_x, L_z]\,\hat{L}_x$$

Using Eq. (6.61) one obtains

$$[\hat{L}_x^2, \hat{L}_z] = -i(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x) \tag{6.63}$$

Similarly one finds

$$[L_y^2, L_z] = i(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x) \tag{6.64}$$

$$[L_z^2, L_z] = 0 \tag{6.65}$$

Thus adding Eqs. (6.63), (6.64) and (6.65,) we obtain

$$[L^2, L_z] = 0 \tag{6.66}$$

Since there is nothing exceptional about the Z-component one can similarly find

$$[L^2, L_x] = [L^2, L_y] = 0 \tag{6.67}$$

The physical significance of all these commutation relations is evident. Since $\hat{L}^2$ commutes with any component of $\hat{L}$ and since the components of $\hat{L}$ do not commute with each other, we conclude that the total angular momentum and only one of its components are simultaneously well defined and observable. It is conventional to choose wave functions of an atom such that L_z is this component. If we perform an experiment to measure the values of $\hat{L}^2$ and $\hat{L}_z$ by applying a magnetic field in the Z-direction and looking at the absorption of light by the atom, then in this experiment the values of x- and y-components of angular momentum are not well defined. This is consistent with the uncertainty principle. Because the knowledge of all the three components of angular momentum with certainty tells us the precise location of the axis of rotation along which the linear momentum is zero. Thus, the magnitude of the linear momentum parallel to this axis is precisely known. On the other hand, for a system whose wave function is known the product of the uncertainty in linear momentum in any direction and the uncertainty in location in the same direction cannot vanish.

6.8 Step-up and Step-down Operators for Angular Momentum

Instead of $\hat{L}_x$ and $\hat{L}_y$, it is usually more convenient to write the complex combination $(\hat{L}_x \pm i\hat{L}_y)$ of these operators. They are called step-up and step-down operators. We denote these two operators by the symbols

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \tag{6.68}$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

Then

$$\hat{L}_z\hat{L}_+ = \hat{L}_z(\hat{L}_x + i\hat{L}_y) = \hat{L}_z\hat{L}_x + i\hat{L}_z\hat{L}_y \tag{6.69}$$

Using the commutation relations (6.60) and (6.61), we can write Eq. (6.69) as

$$\begin{aligned}\hat{L}_z\hat{L}_+ &= \hat{L}_x\hat{L}_z + i\hat{L}_y + i(\hat{L}_y\hat{L}_z - i\hat{L}_x)\\ &= (\hat{L}_x + i\hat{L}_y)\,\hat{L}_z + (\hat{L}_x + i\hat{L}_y)\\ &= \hat{L}_+(\hat{L}_z + 1)\end{aligned} \tag{6.70}$$

Similarly it can be shown that

$$\hat{L}_z\hat{L}_- = \hat{L}_-(\hat{L}_z - 1) \tag{6.71}$$

Since $Y_{l,m}$ are the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ [Eq. (6.56)] consider the operation of $\hat{L}_z$ on $\hat{L}_+Y_{l,m}$. The use of Eq. (6.70) leads to

$$\begin{aligned}\hat{L}_z(\hat{L}_+Y_{l,m}) &= \hat{L}_+(\hat{L}_z + 1)\,Y_{l,m}\\ &= (m+1)\,(\hat{L}_+Y_{l,m})\end{aligned} \tag{6.72}$$

Similarly,

$$\hat{L}_z(\hat{L}_-Y_{l,m}) = (m-1)\,(\hat{L}_-Y_{l,m}) \tag{6.73}$$

Thus we demonstrate that $\hat{L}_+$ and $\hat{L}_-$ are the step-up and step-down operators with respect to the eigenvalue of $\hat{L}_z$. The $\hat{L}_+Y_{l.m}$ is an eigenvector of $\hat{L}_z$ with eigenvalue (i.e. $m + 1$) one unit greater and $L_-Y_{l,m}$ an eigenvector of $\hat{L}_z$ with eigenvalue (i.e. $m - 1$) one unit less, than the eigenvalue of $Y_{l,m}$ itself. That is why the operators $\hat{L}_+$ and $\hat{L}_-$ are also called ladder operators as the successive application of $\hat{L}_+$ (or $\hat{L}_-$) creates a ladder of eigenstates of $\hat{L}_z$. Thus, one may write

$$\hat{L}_+Y_{l,m} = C_+Y_{l,m+1} \tag{6.74a}$$

$$\hat{L}_-Y_{l,m} = C_-Y_{l,m-1} \tag{6.74b}$$

where C_+ and C_- are the numerical constants to be found shortly. However, this ladder cannot extend indefinitely because the value of m is limited by the condition $-l \leqslant m \leqslant l$, according to which the maximum and minimum values of m are $+l$ and $-l$ respectively. Therefore, an attempt to raise the state $Y_{l,m'}$ (where $m' = +l$) must give zero, as there is no state whose eigenvalue for $\hat{L}_z$ is $l + 1$ for a given value of l. Thus,

$$\hat{L}_+Y_{l,l} = 0 \tag{6.75}$$

Similarly one finds

$$\hat{L}_-Y_{l,-l} = 0 \tag{6.76}$$

as there is no state whose eigenvalue for $\hat{L}_z$ is $-(l + 1)$ for given l. Therefore, when m has its lowest possible value, $\hat{L}_-$ annihilates the rotating electron and similarly when m has the maximum value, $\hat{L}_+$ annihilates it.

Now, we shall find the values of C_+ and C_- in Eqs. (6.74a) and (6.74b). In order to determine them we make use of the requirement that the functions $Y_{l,m}$ are normalised. Multiply the left hand side of Eq. (6.74a) with the complex conjugate of $\hat{L}_+ Y_{l,m}$ and integrate over all space. One obtains

$$\langle \hat{L}_+ Y_{l,m} \mid \hat{L}_+ Y_{l,m} \rangle = \mid C_+ \mid^2 \langle Y_{l,m+1} \mid Y_{l,m+1} \rangle = \mid C_+ \mid^2 \tag{6.77}$$

Employing the definition of $\hat{L}_+$ [Eq. (6.68)], the left hand side of Eq. (6.77) may be written as

$$\langle [(\hat{L}_x + i\hat{L}_y)\, Y_{l,m}] \mid L_x \mid Y_{l,m} \rangle + i \langle [(\hat{L}_x + i\hat{L}_y)\, Y_{l,m}] \mid L_y \mid Y_{l,m} \rangle$$

Since the operators $\hat{L}_x$ and $\hat{L}_y$ are hermitian, one may rewrite the above integrals as[3]

$$\langle Y_{l,m} \mid L_x \mid [(\hat{L}_x \pm i\hat{L}_y)\, Y_{l,m}] \rangle^* + i \langle Y_{l,m} \mid L_y \mid [(\hat{L}_x + i\hat{L}_y)\, Y_{l,m}] \rangle^*$$

Noting that

$$(\hat{L}_x + i\hat{L}_y)^* = \hat{L}_x^* - i\hat{L}_y^*$$

one obtains in integral notation

$$\begin{aligned}
&\int Y_{l,m}\ \hat{L}_x^* (\hat{L}_x^* - i\hat{L}_y^*)\, Y_{l,m}^*\, d\tau + i \int Y_{l,m} \hat{L}_y^* (\hat{L}_x^* - i\hat{L}_y^*)\, Y_{l,m}^*\, d\tau \\
&= \int Y_{l,m} [\hat{L}_x^{*2} + \hat{L}_y^{*2} + i(\hat{L}_y^* \hat{L}_x^* - \hat{L}_x^* \hat{L}_y^*)]\, Y_{l,m}^*\, d\tau \\
&= \int Y_{l,m} [\hat{L}_x^{*2} + \hat{L}_y^{*2} - \hat{L}_z^*]\, Y_{l,m}^*\, d\tau
\end{aligned} \tag{6.78}$$

Since

$$L^{*2} = L_x^{*2} + L_y^{*2} + L_z^{*2} = L^2$$

one may write the integral in Eq. (6.78) in bracket notation as

$$\begin{aligned}
&\langle Y_{l,m} \mid (L^2 - L_z^2 - L_z) \mid Y_{l,m} \rangle^* \\
&= \langle Y_{l,m} \mid L^2 \mid Y_{l,m} \rangle^* - \langle Y_{lm} \mid L_z^2 \mid Y_{l,m} \rangle^* - \langle Y_{l,m} \mid L_z \mid Y_{l,m} \rangle^*
\end{aligned} \tag{6.79}$$

Remembering that the functions $Y_{l,m}$ are normalised and the operators hermitian, and after making the obvious substitutions from Eq. (6.56) we have

$$\begin{aligned}
\mid C_+ \mid^2 &= l(l+1) - m^2 - m \\
&= l(l+1) - m(m+1)
\end{aligned} \tag{6.80}$$

Similarly one finds

$$\mid C_- \mid^2 = l(l+1) - m(m-1) \tag{6.81}$$

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[3] According to the turn-over rule (Sec. 2) for a hermitian operator $\hat{A}$,

$$\langle \psi_1 \mid A \mid \psi_2 \rangle = \langle \psi_2 \mid A \mid \psi_1 \rangle^*$$

so that

$$\hat{L}_+ Y_{l,m} = \sqrt{l(l+1) - m(m+1)}\, Y_{l,m+1} \tag{6.82a}$$

$$\hat{L}_- Y_{l,m} = \sqrt{l(l+1) - m(m-1)}\, Y_{l,m-1} \tag{6.82b}$$

These relations are very useful because knowing one eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues l and m one can construct the corresponding eigenfunction having same l and either $m + 1$ or $m - 1$. It may be interesting to find the relation between $\hat{L}_+$, $\hat{L}_-$ and $\hat{L}^2$. We have

$$\begin{aligned}
\hat{L}_+\hat{L}_- &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) \\
&= \hat{L}_x^2 + \hat{L}_y^2 + i\hat{L}_y\hat{L}_x - i\hat{L}_x\hat{L}_y \\
&= \hat{L}_x^2 + \hat{L}_y^2 + i(-i\hat{L}_z) \\
&= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z
\end{aligned}$$

Therefore

$$\hat{L}^2 = \hat{L}_+\hat{L}_- - \hat{L}_z + \hat{L}_z^2 \tag{6.83}$$

Similarly, it can be shown that

$$\hat{L}^2 = \hat{L}_-\hat{L}_+ + \hat{L}_z + \hat{L}_z^2 \tag{6.84}$$

6.9 Angular Momenta in Many-Electron Atom

When there are several electrons in an atom the total orbital angular momentum is obtained by adding together the like component for each electron and then summing the squares of the total components. Let $\hat{l}_{xi}$, $\hat{l}_{yi}$ and $\hat{l}_{zi}$ be the operators for the three components for electron i then total $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ operators are defined for the n-electrons as

$$\begin{aligned}
\hat{L}_x &= \sum_i^n \hat{l}_{xi} \\
\hat{L}_y &= \sum_i^n \hat{l}_{yi} \\
\hat{L}_z &= \sum_i^n \hat{l}_{zi}
\end{aligned} \tag{6.85}$$

Therefore

$$\begin{aligned}
\hat{L}^2 &= (\hat{l}_{x1} + \hat{l}_{x2} + \ldots)^2 + (\hat{l}_{y1} + \hat{l}_{y2} + \ldots)^2 + (\hat{l}_{z1} + \hat{l}_{z2} + \ldots)^2 \\
&= \hat{l}_1^2 + \hat{l}_2^2 + \hat{l}_3^2 \ldots 2\hat{l}_{z1}\hat{l}_{z2} + 2\hat{l}_{z1}\hat{l}_{z3} + \ldots \\
&\quad + (\hat{l}_{+1}\hat{l}_{-2} + \hat{l}_{-1}\hat{l}_{+2}) + \ldots \\
&= \Sigma\, \hat{l}_i^2 + 2 \sum_{i>j} \hat{l}_{zi}\hat{l}_{zj} + \sum_{i>j} (\hat{l}_{+i}\hat{l}_{-j} + \hat{l}_{-i}\hat{l}_{+j})
\end{aligned} \tag{6.86}$$

where
$$\hat{l}_j^2 = \hat{l}_{xj}^2 + \hat{l}_{yj}^2 + \hat{l}_{zj}^2$$
$$\hat{l}_{+j} = \hat{l}_{xj} + i\hat{l}_{yj} \tag{6.87}$$
$$\hat{l}_{-j} = \hat{l}_{xj} - i\hat{l}_{yj}$$

It is very unfortunate that i, and j are used to label electrons while the imaginary quantity $i\,(= \sqrt{-1})$ is also introduced in the definitions of $\hat{l}_{+i}$ and $\hat{l}_{-i}$ operators of the i^{th} electron.

For a many-electron atom, we may write the eigenvalue equations as

$$\hat{L}^2 Y_{L,M_L} = L(L+1)Y_{L,M_L} \tag{6.88}$$

$$\hat{L}_z Y_{L,M_L} = M_L Y_{L,M_L}$$

with $-L \leqslant M_L \leqslant L$
where Y_{L,M_L} are the functions of θ, and ϕ for many electrons, L and M_L are the quantum numbers analogous to l and m of an one-electron atom.

In Chapter 4 (Sec. 4.12) we have mentioned that electron has the spin angular momentum. The various components of spin angular momentum are represented by a set of operators $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$ and S^2 which are analogous to $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ and $\hat{L}^2$ and obey the similar commutation rules.

Let us denote by α, the spin eigenfunction corresponding to $\lambda = +\frac{1}{2}$ and by β, the spin eigenfunction corresponding to $\lambda = -\frac{1}{2}$. Then these functions satisfy the following equations in atomic units.

$$\hat{S}_z\alpha = \tfrac{1}{2}\alpha \qquad \hat{S}_z\beta = -\tfrac{1}{2}\beta$$
$$\hat{S}^2\alpha = \tfrac{1}{2}(\tfrac{1}{2}+1)\alpha \qquad \hat{S}^2\beta = \tfrac{1}{2}(\tfrac{1}{2}+1)\beta \tag{6.89}$$

and

$$\hat{S}_{+\alpha} = (\hat{S}_x + i\hat{S}_y)\alpha = 0$$
$$\hat{S}_{-\alpha} = (\hat{S}_x - i\hat{S}_y)\alpha = \beta$$
$$\hat{S}_{+\beta} = (\hat{S}_x + i\hat{S}_y)\beta = \alpha \tag{6.90}$$
$$\hat{S}_{-\beta} = (\hat{S}_x - i\hat{S}_y)\beta = 0$$

We will have a set of commutation relations analogous to those given in Eqs. (6.59)–(6.61), i.e.

$$[S_x, S_y] = i\hat{S}_z$$
$$[S_y, S_z] = i\hat{S}_x \tag{6.91}$$
$$[S_z, S_x] = i\hat{S}_y$$

as well as analogous to the relations in Eqs. (6.66) and (6.67), viz.

$$[S^2, S_x] = [S^2, S_y] = [S^2, S_z] = 0 \tag{6.92}$$

In an n-electron atom, the n-electron spin operators can be defined as

$$S_x = \sum_i^n \hat{S}_{xi},\ \hat{S}_y = \sum_i^n \hat{S}_{yi},\ \hat{S}_z = \sum_i^n \hat{S}_{zi}$$

and

$$\hat{S}^2 = S_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{6.93}$$

The operators $\hat{S}^2$ and $\hat{S}_z$ satisfy the following eigenvalue equations:

$$\hat{S}^2 f(\theta, \phi, s) = S(S+1)\, f(\theta, \phi, s)$$

$$\hat{S}_z f(\theta, \phi, s) = M_s f(\theta, \phi, s) \tag{6.94}$$

where $-S \leqslant M_s \leqslant S$

where $f(\theta, \phi, s)$ are many-electron wavefunctions containing θ, ϕ and the spin coordinates s. S and M_S are analogous to L and M_L of Eq. (6.88).

The total angular momentum of a single electron in an atomic orbital is represented by an operator j defined as

$$\hat{j}_i = \hat{l}_i + \hat{s}_i \tag{6.95}$$

where l_i and s_i are added vectorially, i.e.

$$\hat{j}_{xi} = \hat{l}_{xi} + \hat{s}_{xi}$$

$$\hat{j}_{yi} = \hat{l}_{yi} + \hat{s}_{yi} \tag{6.96}$$

$$\hat{j}_{zi} = \hat{l}_{zi} + \hat{s}_{zi}$$

And for many-electron atom

$$\hat{J}_x = \sum_i \hat{J}_{xi},\ \hat{J}_y = \sum_i j_{yi},\ \hat{J}_z = \sum_i \hat{j}_{zi}$$

$$J^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \tag{6.97}$$

The operators $\hat{J}^2$ and $\hat{J}_z$ can be shown to satisfy the eigenvalue equation

$$\hat{J}^2\Phi = J(J+1)\Phi$$

$$\hat{J}_z\Phi = M_J\Phi \tag{6.98}$$

with

$$-J \leqslant M_J \leqslant J$$

where Φ is a function of θ and ϕ coordinates as well as the spin coordinate of many electrons, J is the total angular momentum quantum number which is an integer for even number of electrons or a half integer for odd number of electrons. The eigenvalue M_J has the values from $-J, -J+1, \ldots +J$, in other words M_J has $(2J+1)$ different values.

6.10 Commutation with the Hamiltonian

Although the angular momentum operators are time-independent, the expectation values of angular momenta may vary with time if wave functions are time-dependent. To show whether or not the various angular momenta are constants of motion it is necessary to study the commutability of the various angular momentum operators with the hamiltonian.

The operators like $\hat{S}^2$, $\hat{S}_z$ obviously commute with a hamiltonian H [Eq. (6.3)] which does not contain the spin-coordinates. If the hamiltonian of a many-electron atom is of the central field type in which case the electron repulsion is neglected, i.e.

$$\hat{H}_0 = -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} = \sum_i \hat{H}_i \tag{6.99}$$

then $\hat{L}_z$ will obviously commute with $\hat{H}_0$, because $\hat{H}_i$ in spherical polar coordinates is of the form

$$\hat{H}_i = -\tfrac{1}{2}\left[\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial}{\partial r_i}\right) + \frac{1}{r_i^2 \sin\theta}\frac{\partial}{\partial\theta_i}\left(\sin\theta_i\frac{\partial}{\partial\theta_i}\right) + \frac{1}{r_i^2\sin^2\theta_i}\frac{\partial^2}{\partial\phi_i^2}\right] - \frac{Z}{r_i} \tag{6.100}$$

and $\hat{L}_z$ for the many-electron atom is of the form:

$$\hat{L}_z = -\frac{1}{i}\sum_j \frac{\partial}{\partial\phi_j} \tag{6.101}$$

Since θ, ϕ and r are three independent coordinates and $\partial/\partial\phi$ commutes with $\partial^2/\partial\phi^2$, one can conclude that $\hat{L}_z$, and hence $\hat{L}_z^2$ commute with the central field hamiltonian $\hat{H}_0$. To show that $\hat{L}_z$ commutes with $\hat{H}$ of Eq. (6.3) which may be written as

$$\hat{H} = \hat{H}_0 + \tfrac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} \tag{6.102}$$

it is to be shown that $\hat{L}_z$ commutes with the terms like $\hat{1}/r_{ij}$. In Fig. 6.3 is shown how the distance r_{ij} depends on ϕ_i and ϕ_j. One can write

$$\begin{aligned}\left(\frac{\partial}{\partial\phi_i} + \frac{\partial}{\partial\phi_j} + \ldots\right)\frac{1}{r_{ij}} &= \frac{\partial}{\partial(\phi_j - \phi_i)}\left[\frac{1}{r_{ij}}\right]\left\{\frac{\partial(\phi_j - \phi_i)}{\partial\phi_i} + \frac{\partial(\phi_j - \phi_i)}{\partial\phi_j}\right\}\\ &= \frac{\partial}{\partial(\phi_j - \phi_i)}\left[\frac{1}{r_{ij}}\right](-1 + 1)\\ &= 0\end{aligned} \tag{6.103a}$$

Similarly one can show

$$\frac{1}{r_{ij}}\left[\frac{\partial}{\partial\phi_i} + \frac{\partial}{\partial\phi_j} + \ldots\right] = 0 \tag{6.103b}$$

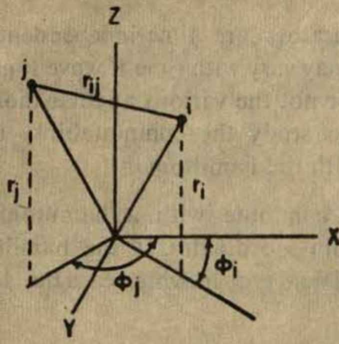

Fig. 6.3 *The interelectronic distance* r_{ij} *as a function of* ϕ_i *and* ϕ_j

Therefore

$$[L_z, H] = 0 \tag{6.104}$$

Thus, $\hat{L}_z^2$ also commutes with $\hat{H}$. Since there is nothing exceptional about the Z-direction $\hat{L}_x^2$, $\hat{L}_y^2$ and hence $\hat{L}^2$ should commute with $\hat{H}$., i.e.

$$[L_z^2, H] = [L_x^2, H] = [L_y^2, H] = [L^2, H] = 0 \tag{6.105}$$

Thus, total orbital angular momentum and one of its components are conserved in a many-electron atom. In a system where the angular momentum is not conserved it does not have definite values in stationary states. Generally, for a system which is in an external field the angular momentum is not conserved. It will be shown in a later chapter that in an axially symmetric field (linear molecule) the component of angular momentum along the axis of symmetry but not the total orbital angular momentum is conserved and therefore the component of angular momentum along the axis of symmetry has definite values. In a non-linear molecule neither $\hat{L}^2$ nor any component of $\hat{L}$ commutes with the molecular hamiltonian and therefore the precise values of angular momentum in this case are not known. Thus, if the hamiltonian of a many-electron atom does not contain terms depending on the spin coordinates then the hamiltonian commutes with all the total spin and total orbital angular momentum operators. Wavefunctions can then be chosen to be eigenfunctions of any mutually commuting set of operators. For instance, $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$ and $\hat{J}_z$ commute with one another and therefore we choose wave functions which are simultaneously eigenfunctions of all these operators. The eigenvalues (or quantum numbers) which are used to label these wave functions are L, M_L, S, M_S and M_J.

6.11 Spin-Orbit Interaction

In addition to the electrostatic interaction between electrons there exists in an atom an interaction between the magnetic field arising from the orbital motion of the electron and the magnetic moment arising from the intrinsic angular momentum of the electron. For an observer, sitting on the nucleus in an atom, the electron moves round the nucleus with a velocity, say v. If, however, an observer sits on the electron and looks at the nucleus in the same atom he will see that the nucleus moves in an orbit around the electron with a velocity $-v$. Since the nucleus bears a positive charge, say Ze, the electron 'sees' itself in the middle of the coil of a wire carrying a current. This current causes a magnetic field which is perpendicular to the plane of the orbit at the position of the electron. Since the electron possesses a magnetic moment due to its intrinsic angular momentum, its energy will depend on the relative orientation of this magnetic moment and the magnetic field arising from the apparent motion of the nuclear charge. Therefore, the energy of an atom depends to some extent on the relalive orientations of the spin-axis and the axis of the orbital angular momentum of the same electron. This spin-orbit coupling splits the multiplet states of atoms and is responsible for the so-called fine-structure in atomic spectra.

We shall follow here an elementary but inexact method to derive an expression for the contribution of the spin-orbit interaction to the atomic hamiltonian. According to Biot-Savart law, the magnetic induction $\boldsymbol{B}$ (in electromagnetic units) at a point arising from current i flowing in a wire of length ds is given by[4] (Slater and Frank).

$$\boldsymbol{B} = \frac{i\,ds \times \boldsymbol{r}}{|r^3|} \tag{6.106}$$

where $\boldsymbol{r}$ is the radius vector of the point from the wire. The current element arising from the apparent motion of the nuclear charge in an atom is given by

$$i\,ds = -zev \tag{6.107}$$

Hence, the magnetic induction acting on the electron is given by

$$\boldsymbol{B} = -\frac{Zev \times \boldsymbol{r}}{|r^3|} = \frac{Ze\cdot \boldsymbol{l}}{m_e|r^3|} \tag{6.108}$$

where $\boldsymbol{l}$ is the angular momentum vector of the electron (i.e. $\boldsymbol{r} \times m_e v$). Expressed in electrostatic units the magnetic induction is

$$\boldsymbol{B} = \frac{Ze\hat{l}}{m_e c|r^3|} \tag{6.109}$$

where for quantum mechanical purposes we have replaced the vector $\boldsymbol{l}$ with an operator $\hat{l}$. We have seen in Chapter 4 [Eq. (4.104)] that the spin-magnetic moment of an electron, μ is related to its intrinsic angular momentum $\hat{s}$ by the relation

$$\mu = -g\frac{e}{2m_e c}\hat{s} \tag{6.110}$$

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[4] J.C. Slater and N.H. Frank, *Electromagnetism*, McGraw-Hill Book Company, Inc., 1947.

The energy of a magnetic dipole in a magnetic field is

$$\varDelta E = -\mu \cdot B = g\frac{Ze^2}{2m_e^2c^2}\frac{\hat{l}\cdot\hat{s}}{|r^3|} \tag{6.111}$$

A rigorous theory which takes into account the relativity effect on the precession of the spin-axis in a magnetic field leads to half this value:

$$\varDelta E = g\cdot\frac{Ze^2\cdot 1}{4m_e^2c^2\,|r^3|}\;\hat{l}\cdot\hat{s}. \tag{6.112}$$

Therefore, from Eq. (6.112) we obtain for the contribution of the spin-orbit interaction to the hamiltonian of a many-electron atom,

$$\hat{H}_{s.o} = \sum_i \xi(i)\hat{l}_i\cdot\hat{s}_i \tag{6.113}$$

where

$$\xi(i) = g\cdot\frac{Ze^2}{4m_e^2c^2}\left|\frac{1}{r_i^3}\right| \tag{6.114}$$

In this spin-orbit interaction term the interaction of the i^{th} electron with the orbital angular momentum of the j^{th} electron is neglected. This is a valid approximation as long as the central field is stronger than the non-spherical part of the interelectronic repulsion terms.

We shall now investigate the commutation of the operators $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$ with $\hat{H}_{s.o}$. Since $\xi(i)$ does not affect the commutation properties we shall deal with the term $\sum_i \hat{l}_i\cdot\hat{S}_i$ which is proportional to $\hat{L}\cdot\hat{S}$. One can write

$$\hat{L}.\hat{S}. = \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z \tag{6.115}$$

Therefore,

$$\hat{L}_z(\hat{L}.\hat{S}.) = \hat{L}_z\hat{L}_x\hat{S}_x + \hat{L}_z\hat{L}_y\hat{S}_y + \hat{L}_z^2\hat{S}_z \tag{6.116a}$$

$$(\hat{L}.\hat{S}.)\hat{L}_z = \hat{L}_x\hat{S}_x\hat{L}_z + \hat{L}_y\hat{S}_y\hat{L}_z + \hat{L}_z\hat{S}_z\hat{L}_z \tag{6.116b}$$

Since the components of $\hat{L}$ are independent of the components of $\hat{S}$ as the spin and orbital coordinates are independent of each other, one obtains from Eq. (6.116)

$$\begin{aligned}[L_z, L.S.] &= (\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z)\,\hat{S}_x + (\hat{L}_z\hat{L}_y - \hat{L}_y\hat{L}_z)\,\hat{S}_y \\ &= i(\hat{L}_y\hat{S}_x - \hat{L}_x\hat{S}_y)\end{aligned} \tag{6.117}$$

In a similar fashion one obtains

$$[S_z, L.S.] = i(\hat{S}_y\hat{L}_x - \hat{S}_x\hat{L}_y) = i(\hat{L}_x\hat{S}_y - \hat{L}_y\hat{S}_x) \tag{6.118}$$

Thus, neither $\hat{L}_z$ nor $\hat{S}_z$ commutes with $\hat{L}.\hat{S}$. If we add Eqs. (6.117) and (6.118), we obtain

$$[L_z + S_z, L.S.] = 0 \tag{6.119}$$

In other words $\hat{J}_z$ commutes with $\hat{H}_{s.o.}$ Therefore $\hat{J}_z^2$, hence $\hat{J}^2$ commutes with $H_{s.o.}$ Thus $\hat{J}_z$ and J^2 and not $\hat{L}^2$, $\hat{S}^2$ or their components commute with the complete hamiltonian that includes the spin-orbit interaction term. The total angular momentum $\hat{J}$ is therefore a constant of motion even though total L and total S may vary with time.

If the spin-orbit coupling is very small as it is very often true with light atoms, then the energy levels and wavefunctions of the complete hamiltonian including $\hat{H}_{s.o}$ will approximate those of the approximate hamiltonian without $\hat{H}_{s.o.}$ The wave functions can then approximately be described by the quantum numbers L and S (although M_L and M_S are not). The spin-orbit interaction energy can then be calculated employing the first order perturbation theory using $H_{s.o}$ as the perturbation hamiltonian. This represents a type of coupling called Russell-Saunders coupling.

For very heavy atoms with large atomic number, the spin-orbit coupling may be large compared to electron-repulsion terms in the hamiltonian $\hat{H}$. In such cases, the interelectronic repulsion term is regarded as a small perturbation, and the unperturbed hamiltonian incorporates $\hat{H}_{s.o.}$ Since neither $\hat{L}^2$ nor $\hat{S}^2$ commutes with such a hamiltonian, the L and S are no longer good quantum numbers to describe the wave functions of this unperturbed hamiltonian. But both $\hat{J}^2$ and $\hat{J}_z$ commute with such hamiltonian and therefore both J and M_J are now good quantum numbers to describe the states of an atom. This type of spin-orbit coupling is known as $j-j$ coupling.

6.12 The Vector Model of the Atom

A given electronic configuration can give rise to a number of states of an atom. The assembly of these states constitutes what is called the multiplet structure of the atom. The detailed quantum mechanical theory of multiplet structure is rather complicated if not difficult. However, a much simpler, though qualitative, approach to the understanding of the multiplet structure is provided by the vector model of the atom. In this model, the total orbital angular momentum of an atom is considered as the vector sum of the quantised angular momenta of the individual electrons.

Let l_1 and l_2 be the quantum numbers which determine the eigenvalues of the operators $\hat{l}_1^2$ and $\hat{l}_2^2$, and m_1 and m_2 determine their projections on the Z-axis. We denote by L and M_L the corresponding quantum numbers for $\hat{L}^2$ and $\hat{L}_z$ of the total orbital angular momentum. To each value of L there are $2L+1$ different values of M_L from $-L$ to $+L$ through zero. The greatest possible value of M_L (for a given l_1 and l_2) is

$$M_L = l_1 + l_2$$

which is obtained when $m_1 = l_1$ and $m_2 = l_2$. Therefore, the atomic states are formed in which the greatest possible value of L and M_L is $l_1 + l_2$. Next, there are two ways in which the value of $M_L = l_1 + l_2 - 1$ is obtained, viz. $m_1 = l_1, m_2 = l_2 - 1$ and $m_1 = l_1 - 1, m_2 = l_2$. Consequently, there must also be two states with these values of M_L. One of them is the state with $L = l_1 + l_2 (M_L = L - 1)$ and the other with $L = l_1 + l_2 - 1$ $(M_L = L)$. Next there are three different ways the value of $M_L = l_1 + l_2 - 2$ is obtained, namely, $m_1 = l_1, m_2 = l_2 - 2$; $m_1 = l_1 - 1, m_2 = l_2 - 1$, and $m_1 = l_1 - 2, m_2 = l_2$. For the value of M_L there are three different states. This means that besides the values $L = l_1 + l_2$, $L = l_1 + l_2 - 1$, the value $L = l_1 + l_2 - 2$ can occur. Carrying on with this argument we arrive at the result that for a given value of l_1 and l_2, the resultant L can take the following values

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, |l_1 + l_2 - 2|, \ldots |l_1 - l_2|$$

Thus there are altogether $2l_2 + 1$ or $2l_1 + 1$ different values of L depending on whether l_2 or l_1 is smaller of the two. There will be, however, $(2l_1 + 1)(2l_2 + 1)$ different values of L, M_L pairs.

This result forms the basis of the vector model of the atom. If we take two vectors l_1 and l_2 of lengths l_1 and l_2 then the values of the resultant vector L are represented by the integral lengths of the vectors L which are obtained by the vector addition of l_1 and l_2. The greatest value of L is $|l_1 + l_2|$ which is obtained when l_1 and l_2 are parallel, and the least value is $|l_1 - l_2|$ when l_1 and l_2 are antiparallel. This addition rule for angular momenta may be extended to add any number, greater than two, of angular momenta by the successive application of this rule.

The resultant values of S (spin angular momentum) and M_s (the component of spin in the Z-direction) are obtained in the same way as the values L and M_L. The energy level having given values of L and S is degenerate. The degree of degeneracy from the directions of L and S is respectively $2L + 1$ and $2S + 1$. Consequently the total degree of the degeneracy of a level with a given value of L and S is equal to $(2L + 1)(2S + 1)$.

If there is a spin-orbit interaction then the orbital angular momentum and the spin angular momentum are no longer separately conserved but the total angular momentum $J = L + S$ is conserved. Then the energy levels of the atom must be characterised by its J values. If the spin-orbit interaction is treated as perturbation, then under the action of this perturbation, a level with a given value of L and S, having $(2L + 1)(2S + 1)$-fold degeneracy is split into a number of distinct levels which have different values of J. This splitting is known as the fine structure or the multiplet splitting. According to the vector addition rule, J takes values from $|L + S|$ to $|L - S|$. Hence a state with a given L and S is split into $2S + 1$ or $2L + 1$ distinct states depending on whether S or L is smaller.

These atomic states are represented by certain symbols (usually called the spectral terms of the atom). The states with different values of L are given the following symbols

$$L = 0, 1, 2, 3, 4 \ldots$$
$$S \; P \; D \; F \; G \ldots$$

To the left above this symbol is placed the number $2S + 1$ as the superior suffix and to the right below this symbol is written the values of J as the inferior suffix. Thus, ${}^2D_{5/2}$, ${}^2D_{3/2}$ denote the atomic states with

$$L = 2, \quad S = \tfrac{1}{2}, \quad J = 5/2 \text{ and } 3/2$$

We shall illustrate with an example how the vector model works. Consider the case of an atom which has two electrons in the valence shell of configuration p^1d^1. It is important to note that the contribution of the inner filled shells to M_L and M_s is zero. The orbital angular momentum for the two electrons is given by

$$L = l_1 + l_2$$

The possible values of L are 3, 2, 1. Thus there are three states F, D and P arising from the p^1d^1 configuration.

Next, we look at the possible values of M_L. For a p-electron we have $m = 1, 0, -1$ and for a d-electron $m = 2, 1, 0, -1, -2$. To obtain the possible values of M_L from these it is convenient to set them out in the form of a table as shown below

		$l = 2$				
$+2$	$+1$	0	-1	-2		
$+3$	$+2$	$+1$	0	-1	$+1$	
$+2$	$+1$	0	-1	-2	0	$l = 1$
$+1$	0	-1	-2	-3	-1	

It is now necessary to construct the values of M_s. Each electron can have the λ values of $+\frac{1}{2}$ and $-\frac{1}{2}$ and the possible resultants are $+1, 0, -1$. The $M_s = 0$ occurs twice because the three other one-electron quantum numbers are not the same and therefore, $\lambda_p = \frac{1}{2}\lambda_d = -1/2$ and $\lambda_p = -1/2$, $\lambda_d = +1/2$ represent two distinguishable spin states.

Starting with the highest value of L (i.e. 3) we take from the Table of M_L values

$$+3, \quad +2, \quad +1, \quad 0, \quad -1, \quad -2, \quad -3$$

This leaves $M_L = \pm 2$ once $M_L = \pm 1, 0$ twice each. For each of the M_L values in $L = 3$ term, each of the four possible spin values can occur. This gives rise to a triplet $(M_s = 1, 0, -1)$ ${}^3F$ and a singlet $(M_s = 0)$ ${}^1F$ terms.

From the remaining M_L values, states with $L = 2$ can be found. For this, the values of M_L are as follows.

$$+2, \quad +1, \quad 0, \quad -1, \quad -2$$

This leaves $M_L = \pm 1, 0$ once. Therefore D state can occur both as a triplet and a singlet. From the remaining M_L terms two P states can be formed

(^1P, ^3P). Thus the possible states which arise from the p^1d^1 configuration are

$$^1F,\ \ ^3F,\ \ ^1D,\ \ ^3D,\ \ ^1P,\ \ ^3P$$

These terms all have the different energies because of the electron repulsion. There is a rule known as Hund's rule which predicts which term is most stable. This rule states that a state of maximum multiplicity has the lowest energy and if the two terms have the same multiplicity, the one with the larger value of L has the lower energy. Thus, of all the six terms, ^3F has the lowest energy.

Now the spin-orbit interaction will split the above terms into a number of fine structure components. Each fine structure component is characterised by its J value. For example, ^3F term has $L = 3$, $S = 1$. Possible values of J are $3 + 1, 4 - 1, 4 - 2$ (i.e. $3 - 1$), or 4, 3, 2. Thus, there are $^3F_4$, $^3F_3$ and $^3F_2$ fine-structure components of the ^3F term. Similarly ^3D has $^3D_3$, $^3D_2$, $^3D_1$ and ^3P has $^3P_2$, $^3P_1$, $^3P_0$ fine structure components, while the singlet terms are not split. Each fine structure component is $(2J + 1)$-fold degenerate in the absence of an external field.

There is another Hund's rule which states that if a term arises from a configuration with less than a half filled shell, then after the spin-orbit coupling the level with the lowest value of J has the lowest energy. This is called the normal multiplet. If the configuration has more than a half filled shell then the level of highest J has the lowest energy. This is called the inverted multiplet. Therefore, the p^1d^1 configuration has the lowest level represented by $^3F_2$.

Finally, we shall briefly outline how the hyperfine structure of the levels arise. The hyperfine structure of the atomic level arises from the nuclear spin described by the spin quantum number I. The interaction of the nuclear spin with the electrons is very weak and hence the splitting which it causes is very small. A level with a given angular momentum J is split into a number of hyperfine structure components which differ in the values of total angular momentum F of the atom including its nucleus. F can take the following values according to the vector addition rule.

$$F = |J + I|,\ \ |J + I - 1|,\ \ |J + I - 2|, \ldots |J - I|$$

Each component after the hyperfine splitting is again $(2F + 1)$-fold degenerate in the absence of an external field.

APPENDIX 6

We shall evaluate the following integral

$$J = \langle 1s(1)1s(2) \left| \frac{1}{r_{12}} \right| 1s(1)1s(2) \rangle$$

$$= \frac{Z'^6}{\pi^2} \iint \frac{\exp(-2Z'r_1)\exp(-2z'r_2)}{r_{12}}\, dT_1\, dT_2 \qquad \text{(A6.1)}$$

where

$$dT_1 = r_1^2\, dr_1 \sin\theta_1\, d\theta_1\, d\phi_1$$

$$dT_2 = r_2^2\, dr_2 \sin\theta_2\, d\theta_2\, d\phi_2$$

This integral represents the potential energy of interaction of two overlapping spheres of charge cloud of densities $\rho_1 = \exp(-2z'r_1)$ and $\rho_2 = \exp(-2z'r_2)$ throughout the whole space. This interpretation suggests a relatively simple method of evaluating the integral (A6.1). It is well known that the electric potential inside a uniformly charged sphere is everywhere same as the potential of the shell, whereas the potential outside the shell is calculated by considering that the total charge of the shell is concentrated at the centre of the shell.

To evaluate the integral, consider a spherical shell of radius r_1 and thickness dr_1. Then its total charge is

$$\exp(-2z'r_1)r_1^2\, dr_1 \int_0^{\pi} \sin\theta_1\, d\theta_1 \int_0^{2\pi} d\phi_1$$

$$= 4\pi r_1^2\, dr_1 \exp(-2z'r_1) \tag{A6.2}$$

The potential due to this charge distribution at a distance r from the origin is

$$\begin{aligned} V &= 4\pi r_1^2 \frac{dr_1}{r_1} \cdot \exp(-2z'r_1), \qquad \text{for } r < r_1 \\ &= 4\pi r_1^2 \frac{dr_1}{r} \exp(-2z'r_1), \qquad \text{for } r > r_1 \end{aligned} \tag{A6.3}$$

Hence the potential at r due to the entire cloud is

$$V(r) = 4\pi \int_r^{\infty} r_1 \exp(-2z'r_1)\, dr_1 + \frac{4\pi}{r}\int_0^r \exp(-2z'r_1) r_1^2\, dr_1 \tag{A6.4}$$

On integration by parts, the first term of Eq. (A6.4) gives

$$\frac{2\pi}{z'} \exp(-2z'r)\left(r + \frac{1}{2z'}\right)$$

and the second term Eq. (A6.4) gives

$$-\frac{2\pi}{z'} \exp(-2z'r)\left(r + \frac{1}{z'}\right) - \frac{\pi}{z'^3 r}\left[\exp(-2z'r) - 1\right]$$

Therefore $V(r)$ may be written as

$$V(r) = -\frac{\pi}{z'^2} \exp(-2z'r) - \frac{\pi}{z'^3 r}\left[\exp(-2z'r) - 1\right] \tag{A6.5}$$

The mutual potential energy of interaction of the spherical clouds, which is represented by the integral (A6.1) is given as

$$\begin{aligned} J &= \frac{z'^6}{\pi^2}\int_0^{\infty} V(r_2) \exp(-2z'r_2) r_2^2\, dr_2 \int_0^{\pi} \sin\theta_2\, d\theta_2 \int_0^{2\pi} d\phi_2 \\ &= \frac{z'^6}{\pi^2} \cdot 4\pi \int_0^{\infty} V(r_2) \exp(-2z'r_2) r_2^2\, dr_2 \end{aligned} \tag{A6.6}$$

Substituting for $V(r_2)$ the form of expression given by Eq. (A6.5) in Eq. (A6.6) and employing the following standard integral

$$\int_0^\infty \exp(-ax)x^n\,dx = \frac{n!}{a^{n+1}}$$

The integral (A6.6) can be evaluated as follows:

$$\begin{aligned} J &= \frac{4z'^6}{\pi}\Big[-\frac{\pi}{z'^2}\int_0^\infty \exp(-4z'r_2)r_2^2\,dr_2 \\ &\quad -\frac{\pi}{z'^3}\int_0^\infty \exp(-4z'r_2)r_2\,dr_2 + \frac{\pi}{z'^3}\int_0^\infty \exp(-2z'r_2)r_2\,dr_2\Big] \\ &= -\frac{4z'^6}{z'^2}\frac{2}{(4z')^3} - \frac{4z'^6}{z'^3}\cdot\frac{1}{(4z')^2} + \frac{4z'^6}{z'^3}\cdot\frac{1}{(2z')^2} \\ &= 5/8z' \end{aligned} \tag{A6.7}$$

PROBLEMS

1. Obtain the energy of the ground state of the helium atom employing the first order perturbation theory with the electronic repulsion potential as the perturbation.
2. Show that $\hat{L}_+$ and $\hat{L}_-$ are not but $\hat{L}_-\hat{L}_+$ and $\hat{L}_+\hat{L}_-$ are hermitian.
3. The wave function ($\hat{L} = 2\ M_L = 0$) of a ^1D term resulting from a p^2 configuration is given by

$$\psi(2, 0) = \frac{1}{\sqrt{6}}\{2\,|\phi_0\bar{\phi}_0| + |\phi_1\bar{\phi}_{-1}| + |\phi_{-1}\bar{\phi}_1|\}$$

where ϕ_0, ϕ_1, ϕ_{-1} are the three p orbitals with subscript indicating their m values.

Employing the $\hat{L}_+$ and $\hat{L}_-$ operators, obtain the remaining wave functions belonging to ^1D term.

4. An atom with a single unpaired electron in a d orbital has two fine structure components $^2D_{5/2}$ and $^2D_{3/2}$. The spin-orbit interaction operator for a single electron is given by

$$\xi(r)\hat{L}\cdot\hat{S}$$

Find the energy difference in unit of ξ between the fine structure components.

5. Show that a closed shell electron configuration is always represented by ^1S term.
6. Obtain the term symbol for the ground state of the nitrogen atom assuming the Russell-Saunders coupling.

7

Molecular Orbital and Valence Bond Theories for Diatomic Molecules

7.1 Introduction

When dealing with molecules, the first question a chemist asks: "What is the nature of the force that binds two atoms in a molecule?" This force is so strong that about 60 $\sim$ 100 Kcal/mole of energy is required to break a bond. The first theory of chemical bonding was given by G.N. Lewis in 1916. According to him a chemical bond is formed by sharing a pair of electrons between the two nuclei. But it was not clear then how the electron-sharing took place in an electron-pair bond. The next question one may ask: "Like the electron in a hydrogen atom, does the electron in H_2^+ have a series of distinct quantum states?" Besides, in molecules one has to deal with not only the moving electrons but also the moving nuclei. Therefore drastic approximations must be made in solving the Schrodinger equation for a many-electron molecule. A great deal of imagination is needed to obtain approximate but meaningful solutions of the wave equation for molecules.

Historically, two approaches emerged: (i) the molecular orbital and (ii) the valence-bond approximations. Of these, the concept of the molecular orbital theory is most simple mathematically and therefore widely used for treatment of poly-atomic molecules in chemistry. The general concept of molecular orbitals and of the building-up principle using molecular orbitals were developed in 1927 by Hund and Mulliken and in 1929 by Lennard Jones. Their method of molecular orbitals is characterised by its fundamental simplicity and its ability to predict and explain certain chemical properties like paramagnetism of O_2 and NO and many other features of the structure and spectra of diatomic molecules with a reasonable degree of accuracy. More striking than these is the experimental verification of the energy ordering of the molecular orbitals (MO) of molecules by photoelectron spectroscopy. The Hartree-Fock approximation, which has been useful in atoms can be extended to molecules within the framework of the molecular orbital theory. In this chapter we shall deal with both approximations for treatment of the homo- and hetero-nuclear diatomic molecules.

Whether we deal with the valence-bond (VB) or molecular-orbital (MO) approach we have to deal with electrons and nuclei. Since an electron is a light particle compared to the mass of a proton (the mass of a proton is 1836 times as great as the mass of an electron) the nuclei are expected to move much more slowly than the electrons. The electrons in a molecule may have an average distribution over a time during which the nuclei hardly move. This argument was first put forward by Born and Oppenheimer in 1927[1]. This means that the vibrational and rotational motions of a molecule are separable from the electronic motions. Before taking up the MO and VB theories we shall first treat the Born-Oppenheimer approximation in wave-mechanical terms.

7.2 The Born-Oppenheimer Approximation

The hamiltonian for a system of nuclei (μ, ν, . . .) and electrons ($i, j, \ldots$) is as follows:

$$H(r, R) = -\sum_{\mu} \frac{h^2}{8\pi^2 M_\mu} \nabla\mu^2 - \sum_{i} \frac{h^2}{8\pi^2 m_e} \nabla i^2 + V_{ne}(r, R) + V_{ee}(r) + V_{nn}(R) \quad (7.1)$$

where r and R are the electronic and nuclear coordinates, V_{ne} the nuclear-electron attraction, V_{ee} the electron-electron repulsion and V_{nn} the nuclear-nuclear repulsion terms. If we separate off the nuclear kinetic energy terms from the rest of the terms

$$H(r, R) = H_n(R) + H_e(r, R) \quad (7.2)$$

where

$$H_n(R) = -\sum_{\mu} \frac{h^2}{8\pi^2 M_\mu} \nabla\mu^2 \quad (7.3)$$

and

$$H_e(r, R) = H(r, R) - H_n(R) \quad (7.4)$$

then $H_e(r, R)$ describes the motion of electrons in the fixed nuclear framework. Since nuclear masses (M_μ) are very much greater than electronic mass we expect nuclei to move much more slowly than electrons. Electrons can, therefore, be assumed to respond to the nuclear motion almost instantaneously. Instead to trying to solve a wave equation for moving nuclei and moving electrons, we may assume nuclei to be fixed in a particular conformation and solve the equation

$$H_e(r, R)\, \psi_e(r, R) = E(R)\psi_e(r, R) \quad (7.5)$$

where $E(R)$ and $\psi_e(r, R)$ are the energy and the electronic wave function for a particular fixed nuclear framework respectively. Now, we change the nuclear coordinate, R (R being the internuclear distance in the case of a diatomic molecule) and solve Eq. (7.5) again for the new fixed positions of nuclei. In this way one obtains the energy $E(R)$ as a function of R. Such energy curves are called the adiabatic curves.

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[1] M. Born and K. Huang, *Dynamical theory of crystal lattices*, Clarendon Press, Oxford (1954).

Now we consider the nuclear motion. We use $E(R)$ as a potential energy function to describe the nuclear motion. Therefore, the nuclear wave functions are obtained from the Schrodinger equation of the form

$$[H_n(R) + E(R)]\psi_{\text{nuc}}(R) = \epsilon\cdot\psi_{\text{nuc}}(R) \tag{7.6}$$

where $\psi_{\text{nuc}}(R)$ is the nuclear function and ϵ, the total energy including the nuclear kinetic energy. Thus, if we write the complete wave function as

$$\psi(r, R) = \psi_e(r, R)\cdot\psi_{\text{nuc}}(R) \tag{7.7}$$

then we are able to write the complete wave equation in the following form

$$\begin{aligned} H(r, R)\,\psi(r, R) &= [H_e(r, R) + H_n(R)]\psi_e(r, R)\psi_{\text{nuc}}(R) \\ &= \psi_{\text{nuc}}(R)H_e(r, R)\psi_e(r, R) + \psi_e(r, (R)H_n(R)\psi_{\text{nuc}}(R) \\ &\quad - \psi_{\text{nuc}}(R)\sum_\mu \frac{h^2}{8\pi^2 M_\mu}\nabla^2_\mu\psi_e(r, R) \\ &\quad - \sum_\mu \frac{h^2}{8\pi^2 M_\mu}\,2\,\frac{\partial\psi_e(r, R)}{\partial R_\mu}\,\frac{\partial\psi_{\text{nuc}}(R)}{\partial R_\mu} \\ &= \psi_e(r, R)[H_n(R) + E(R)]\psi_{\text{nuc}}(R) - \left\{\sum_\mu \frac{h^2}{8\pi^2 M_\mu}\right. \\ &\quad \left.\times\left(\psi_{\text{nuc}}(R)\nabla^2_\mu\psi_e(r, R) + 2\,\frac{\partial\psi_e(r, R)}{\partial R_\mu}\,\frac{\partial\psi_{\text{nuc}}(R)}{\partial R_\mu}\right)\right\} \\ &= \epsilon\psi_e(r, R)\psi_{\text{nuc}}(R) - \left\{\sum_\mu \frac{h^2}{8\pi^2 M_\mu}\left(\psi_{\text{nuc}}(R)\nabla^2_\mu\psi_e(r, R)\right.\right. \\ &\quad \left.\left. + 2\,\frac{\partial\psi_e(r, R)}{\partial R_\mu}\,\frac{\partial\psi_{\text{nuc}}(R)}{\partial R_\mu}\right)\right\} \\ &= \epsilon\psi(r, R) - \left\{\sum_\mu \frac{h^2}{8\pi^2 M_\mu}\left(\psi_{\text{nuc}}(R)\nabla^2_\mu\psi_e(r, R)\right.\right. \\ &\quad \left.\left. + 2\,\frac{\partial\psi_e(r, R)}{\partial R_\mu}\,\frac{\partial\psi_{\text{nuc}}(R)}{\partial R_\mu}\right)\right\} \end{aligned} \tag{7.8}$$

The terms within the brackets appearing on the right hand side of Eq. (7.8) are considered negligibly small for a molecule with nondegenerate energy levels and, therefore, the separation of electronic and nuclear motions is possible. Such separation of the nuclear and electronic function describes the adiabatic principle or Born-Oppenheimer approximation, according to which the true wave functions of systems of moving electrons and nuclei will differ very slightly from those calculated in this way. It has been shown by Kolos and Wolniewicz[2] that errors introduced by the Born-Oppenheimer approximation for H_2 is 4.95 cm^{-1} (or 6.2×10^{-4} eV) while the total energy is 32 eV and its dissociation energy is 4.76 eV. Such errors are definitely much smaller than errors involved in the approximate solutions of the electronic Schrodinger equation and can be ignored.

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[2] W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **41**, 3663, 3674 (1964).

7.3 Breakdown of Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is valid as long as the electronic wavefunction of the molecule concerned varies very slowly with its nuclear motion. We shall now examine the condition when this restriction fails. Since $H_e(r, R)$ is also a function of the nuclear coordinates R, for small displacements of the nuclei dR from the equilibrium R_0, one can write according to Taylor's series as

$$H_e(r, R) = H_e(r, R_0) + \left(\frac{\partial H_e}{\partial R}\right)_{R_0}\cdot(dR) + \frac{1}{2}\left(\frac{\partial^2 H_e}{\partial R^2}\right)_{R_0}\cdot(dR)^2 + \ldots \tag{7.9}$$

We shall show later that, as in atoms, electrons in molecules have discrete quantum states. Let us consider the i^{th} electronic state of a molecule, its wavefunction $\psi_{e,i}(r, R)$ must also change with the nuclear displacement dR from the equilibrium value R_0. So one may write Taylor's expansion of $\psi_e(r, R)$ as

$$\psi_{e,i}(r, R) = \psi_{e,i}(r, R_0) + \left(\frac{\partial \psi_{e,i}}{\partial R}\right)_{R_0}\cdot(dR) + \ldots \tag{7.10}$$

We consider the second term of Eq. (7.9) as perturbation

$$H' = \left(\frac{\partial H_e}{\partial R}\right)_{R_0}\cdot(dR)$$

and ignore the subsequent terms as the displacement dR is assumed to be small. Since $\psi_{e,j}(r, R_0)$, $\psi_{e,i}(r, R_0)$ etc., form a complete orthonormal set of zero-order wavefunctions of $H_e(r, R_0)$, we may now apply the first-order perturbation theory to get the wavefunction for the displaced positions of the nuclei. This is given by

$$\psi_{e,i}(r, R) = \psi_{e,i}(r, R_0) + \sum_{j\neq i} \frac{\langle \psi_{e,i}(r, R_0) \mid H' \mid \psi_{e,j}(r, R_0)\rangle}{E_i^0 - E_j^0}\, \psi_{e,j}(r, R_0) \tag{7.11}$$

where E_i^0, E_j^0, etc., are the energies of the i^{th} and j^{th} electronic states of the molecule for the nuclear configuration R_0. Since $\psi_{e,i}(r, R)$ is also given by Eq. (7.10) for small displacement dR, we can write

$$\left(\frac{\partial \psi_{e,i}}{\partial R}\right)_{R_0} dR = \sum_{j\neq i} \frac{\langle \psi_{e,i}(r, R_0) \left| \left(\frac{\partial H_e}{\partial R}\right) \right| \psi_{e,j}(r, R_0) \rangle\, dR}{E_i^0 - E_j^0}\, \psi_{e,j}(r, R_0) \tag{7.12}$$

Since the integration is over the electronic coordinates in the numerator of the right hand side of Eq. (7.12), we have taken out the nuclear coordinates dR. We have

$$\left(\frac{\partial\psi_{e,i}}{\partial R}\right)_{R_0} = \sum_{j\neq i} \frac{\left\langle \psi_{e,i}(r, R_0) \left| \left(\frac{\partial H_e}{\partial R}\right)_{R_0} \right| \psi_{e,j}(r, R_0) \right\rangle}{E_i^0 - E_j^0} \psi_{e,j}(r, R_0) \tag{7.13}$$

Similarly,

$$\left(\frac{\partial^2\psi_{e,i}}{\partial R^2}\right)_{R_0} = \frac{\partial}{\partial R}\left(\frac{\partial\psi_{e,i}}{\partial R}\right)_{R_0}$$

$$= \frac{\partial}{\partial R}\left[\sum_{j\neq i} \frac{\left\langle \psi_{e,i}(r, R_0) \left| \left(\frac{\partial H_e}{\partial R}\right)_{R_0} \right| \psi_{e,j}(r, R_0) \right\rangle}{E_i^0 - E_j^0} \cdot \psi_{e,j}(r, R_0) \right] \tag{7.14}$$

Both Eq. (7.13) and (7.14) reveal that if the molecule has widely separated electronic energy states, i.e., $E_i^0 \neq E_j^0$ and vanishingly small interaction matrix elements between the electronic states, the separation of electronic and nuclear motions is ideally possible. Hence, the Born-Oppenheimer approximation breaks down if the concerned electronic state is degenerate or nearly degenerate with the other electronic states of the molecule. For most molecules, the Born-Oppenheimer approximation is valid for the ground electronic state because the lowest excited state has much higher energy than that of the ground state but in the excited state this approximation may not be valid because the energy separation among the excited levels is small.

7.4 The Molecular Orbital Theory (The LCAO Approximation)

It is assumed that electrons in molecules occupy certain orbitals, which extend over all the nuclei in a molecule. Let us consider the simplest example, i.e., H_2^+ with one electron in it. Consider the two nuclei H_a and H_b. When the electron is near the nucleus *a*, that electron can be adequately described by the wavefunction of the atomic orbital, ϕ_a centred on '*a*'. When the electron is near the nucleus '*b*', we can describe that electron by the atomic orbital ϕ_b on '*b*'. So, for the electron anywhere in H_2^+, Hund and Mulliken assumed that the electron can be described by a function of the form

$$\psi = C_1\phi_a + C_2\phi_b \tag{7.15}$$

where C_1 and C_2 are the atomic orbital coefficients which are so chosen that the energy given by ψ of Eq. (7.15) is minimum. Similarly, for H_3^{+2}, the electron can be described by a function of the form

$$\psi = C_1\phi_a + C_2\phi_b + C_3\phi_c \tag{7.16}$$

where *a*, *b*, and *c* are the three *H*-nuclei in H_3^{+2}. Such description of wavefunction of an electron in a molecule having several atoms is known as the linear combination of atomic orbitals (usually called LCAO). Each atom may contribute several atomic orbitals in the construction of molecular orbitals. For the sake of simplicity we assume that each atom contributes only one orbital in a *n*-atomic molecule. If $\phi_1, \phi_2, \phi_3, \ldots, \phi_n$ be the atomic orbitals on atoms 1, 2, . . . n respectively, the molecular orbitals are approximately written as

$$\psi = \sum_{i=1}^{n} C_i\phi_i \tag{7.17}$$

The electronic energy of this system based on the function (7.17) is given by

$$E = \frac{\langle \sum_i^n C_i\phi_i \mid H_e \mid \sum_i^n C_i\phi_i \rangle}{\langle \sum_i^n C_i\phi_i \mid \sum_i^n C_i\phi_i \rangle} = f(C_1, C_2, \ldots, C_n) \tag{7.18}$$

Since the function ψ in Eq. (7.17) is chosen arbitrarily, the calculated energy of the system, according to the variation theorem, will be always greater than the true minimum energy. The above energy should, therefore, be minimized with respect to the parameters, $C_1, C_2, C_3, \ldots, C_n$. The stationary values of E satisfy

$$\begin{aligned} &\partial E(C_1, C_2, C_3, \ldots C_n) \\ &= \frac{\partial E}{\partial C_1}\partial C_1 + \frac{\partial E}{\partial C_2}\partial C_2 + \frac{\partial E}{\partial C_3}\partial C_3 + \ldots + \frac{\partial E}{\partial C_n}\partial C_n = 0 \end{aligned} \tag{7.19}$$

The solution of the algebraic equations, i.e.,

$$\frac{\partial E}{\partial C_n} = 0, \qquad n = 1, 2, 3, \ldots, n \tag{7.20}$$

will lead to approximations to the energy E_i and the corresponding molecular orbital wavefunction ψ_i for the stationary states. From Eq. (7.18) one can write

$$E = \frac{\sum_i^n C_i^2 H_{ii} + 2\sum_{i>j}^n C_iC_jH_{ij}}{\sum_i^n C_i^2\Delta_{ii} + 2\sum_{i>j}^n C_iC_j\Delta_{ij}} \tag{7.21}$$

where

$$\begin{aligned} H_{ii} &= \langle \phi_i \mid H_e \mid \phi_i \rangle \\ H_{ij} &= \langle \phi_i \mid H_e \mid \phi_j \rangle \\ \Delta_{ij} &= \langle \phi_i \mid \phi_j \rangle \\ \Delta_{ii} &= \langle \phi_i \mid \phi_i \rangle \end{aligned} \tag{7.22}$$

Equation (7.21) may be rearranged as

$$\begin{aligned} &\sum_i^n C_i^2 H_{ii} + 2\sum_{i>j}^n C_iC_jH_{ij} \\ &= E\left[\sum_i^n C_i^2\Delta_{ii} + 2\sum_{i>j}^n C_iC_j\Delta_{ij}\right] \end{aligned} \tag{7.23}$$

Differentiation of Eq. (7.23) with respect to C_i, keeping all other coefficients constant (remembering that H_{ij} and Δ_{ij} are always constants) gives

$$2C_iH_{ii} + 2\sum_{j\neq i} C_jH_{ij} = E\left[2C_i\Delta_{ii} + 2\sum_{j\neq i}^{n} C_j\Delta_{ij}\right] + \frac{\partial E}{\partial C_i}\left[\sum_{i}^{n} C_i^2\Delta_{ii} + 2\sum_{i>j}^{n} C_iC_j\Delta_{ij}\right] \quad (7.24)$$

For an energy minimum, with respect to C_i, $\partial E/\partial C_i = 0$ and we have

$$2C_i(H_{ii} - \Delta_{ii}E) + 2\sum_{j\neq i} C_j(H_{ij} - \Delta_{ij}E) = 0$$

i.e.,

$$\sum_{j}^{n} C_j(H_{ij} - \Delta_{ij}E) = 0 \quad (7.25)$$

Thus, if Eq. (7.23) is minimised with respect to the parameters, C_1, C_2, C_3, . . ., etc., one by one, we obtain the following set of equations known as the secular equations.

$$\left.\begin{aligned} C_1(H_{11} - \Delta_{11}E) + C_2(H_{12} - \Delta_{12}E) + C_3(H_{13} - \Delta_{13}E) + \ldots &= 0 \\ C_1(H_{21} - \Delta_{21}E) + C_2(H_{22} - \Delta_{22}E) + C_3(H_{23} - \Delta_{23}E) + \ldots &= 0 \\ C_1(H_{n1} - \Delta_{n1}E) + C_2(H_{n2} - \Delta_{n2}E) + \ldots + C_n(H_{nn} - \Delta_{nn}E) &= 0 \end{aligned}\right\} \quad (7.26)$$

If this set of n equations is to have non-trivial solutions (i.e., $C_1 \neq 0$, $C_2 \neq 0$, etc.) the determinant of the coefficients C_i must vanish. That is,

$$\begin{vmatrix} H_{11} - \Delta_{11}E & H_{12} - \Delta_{12}E & H_{13} - \Delta_{13}E & \ldots & H_{1n} - \Delta_{1n}E \\ H_{21} - \Delta_{21}E & H_{22} - \Delta_{22}E & \ldots & & H_{2n} - \Delta_{2n}E \\ H_{n1} - \Delta_{n1}E & H_{n2} - \Delta_{n2}E & \ldots & & H_{nn} - \Delta_{nn}E \end{vmatrix} = 0 \quad (7.27)$$

The determinant on the left hand side of Eq. (7.27) is called the secular determinant. Since this equation is of the n^{th} order, in principle it gives n roots, viz., E_1, E_2, . . ., E_n and therefore a set of n wavefunctions ψ_1, ψ_2, . . ., ψ_n respectively.

Thus the LCAO approximation leads to creation of several molecular orbitals (MO) for each molecule. To obtain the wavefunction of the ground state of a molecule, the MOs are fed with electrons starting from the lowest energy, subject to the restriction imposed by the Pauli exclusion principle that not more than two electrons can occupy each MO. This is the basis of the LCAO treatment for calculations of approximate energies and wavefunctions for molecular orbitals in molecules.

It must be mentioned here that in order to generate an effective MO through the LCAO approximation the atomic orbitals must have energies of the comparable magnitude. For example, if ϕ_1 and ϕ_2, the two atomic orbitals have very different energies in a two-atom molecule, the electron will tend to remain most of the time in the atomic orbital which has lower energy in the ground state, while in the excited state it will be found in the atomic orbital which has the higher energy. Thus, virtually no gain is achieved by the LCAO method.

Besides, for effective combination of the atomic orbitals, ϕ_1 and ϕ_2 must overlap. This is possible if ϕ_1 and ϕ_2 have the same symmetry relative to the molecular axis. Consider a *C–H* bond along the *z*-axis. An MO could be formed by linear combination of the $2p_z$ atomic orbital of carbon with the 1*s*-atomic orbital of hydrogen. These two orbitals overlap and according to the LCAO approximation, the MO of a C–H bond is given by

$$\psi_{C-H} = C_1 2p_{z,C} + C_2 1s_H \tag{7.28}$$

where the atomic orbital wavefunctions for the 1*s* and $2p_z$ orbitals are denoted by 1*s* and $2p_z$ respectively. Here, both the 1*s* and $2p_z$-orbitals are symmetric with respect to rotation about the internuclear axis (Fig. 7.1). On the other hand the $2p_x$-orbital of carbon cannot overlap the 1*s*-orbital of hydrogen (Fig. 7.2). Here the $2p_x$-orbital is antisymmetric with respect to rotation about the *z*-axis. Thus, a $2p_x$-orbital cannot combine with the 1*s*-orbital to form a MO. However, a $2p_x$-orbital on a carbon atom can combine with another $2p_x$-orbital centred on a different carbon atom to form a MO, because both have the same symmetry relative to the molecular axis (Fig. 7.3). Such MOs are called the π-molecular orbitals which will be discussed in great detail in a later chapter.

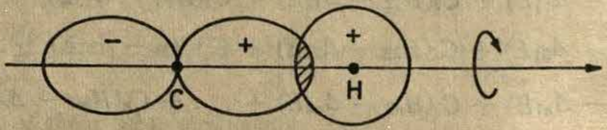

Fig. 7.1 *Overlap between atomic orbitals of same symmetry. The C-H bond is taken as the Z-axis*

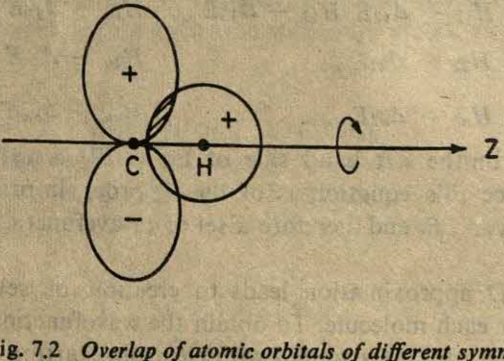

Fig. 7.2 *Overlap of atomic orbitals of different symmetry. The shaded (positive) and the unshaded (negative) parts of the overlap cancel*

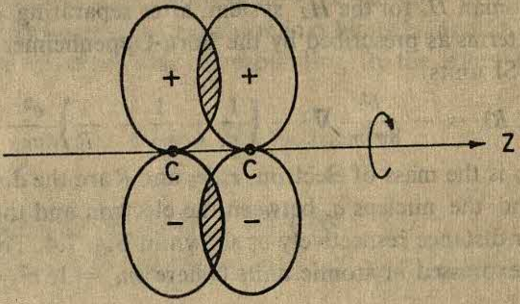

Fig. 7.3 *Overlap of orbitals of same symmetry. Here both atomic orbitals are antisymmetric*

7.5 The Hydrogen Molecule Ion

The system of H_2^+ is composed of two protons and an electron and was discovered many years ago by Thompson in a cathode ray tube. From the spectroscopic studies, the ground state of H_2^+ is known to have the equilibrium internuclear distance of 1.06 Å and a dissociation energy of 2.8 eV. Although the exact solution of the Schrodinger equation for this system is possible, we shall examine this system within the framework of the Born-Oppenheimer approximation and the LCAO-molecular orbital theory as this method has the advantage of providing a valuable insight into the nature of chemical bonding, which is not so readily obtained from the exact solution.

The lowest energy atomic orbital of the hydrogen atom is the 1*s* orbital. We therefore expect the lowest energy molecular orbital (MO) of H_2^+, in the LCAO approximation to be given by

$$\psi = C_1 1s_a + C_2 1s_b \tag{7.29}$$

where the two nuclei are labelled as *a* and *b*, C_1 and C_2 are the parameters to be so adjusted that the calculated energy becomes minimum. This calculation was first performed by Pauling (1928)[3].

The method described in Sec. 7.4 leads to the following secular determinant which is zero for the non-trivial solutions.

$$\begin{vmatrix} H_{aa} - \Delta_{aa}E & H_{ab} - \Delta_{ab}E \\ H_{ba} - \Delta_{ba}E & H_{bb} - \Delta_{bb}E \end{vmatrix} = 0 \tag{7.30}$$

where

$$\begin{aligned} H_{aa} &= \langle 1sa \mid He \mid 1sa \rangle \\ H_{bb} &= \langle 1sb \mid He \mid 1sb \rangle \\ H_{ab} &= H_{ba} = \langle 1sa \mid He \mid 1sb \rangle \\ \Delta_{aa} &= \Delta_{bb} = \langle 1s_b \mid 1s_b \rangle \\ \Delta_{ab} &= \Delta_{ba} = \langle 1s_a \mid 1s_b \rangle \end{aligned} \tag{7.31}$$

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[3] L. Pauling, *Chem. Rev.*, **5**, 173, (1928).

and the hamiltonian H_e for the H_2^+ system, after separating off the nuclear kinetic energy terms as prescribed by the Born-Oppenheimer approximation is given by (in SI units)

$$H_e(r, R) = -\frac{h^2}{8\pi^2 m_e}\nabla^2 - \left(\frac{1}{r_a} + \frac{1}{r_b} - \frac{1}{R}\right)\frac{e^2}{4\pi\epsilon_0} \tag{7.32}$$

In Eq. (7.32) m_e is the mass of electron, r_a, r_b and R are the distances between the electron and the nucleus a, between the electron and the nucleus b and the internuclear distance respectively as shown in Fig. 7.4. The above hamiltonian may be expressed in atomic units (where $m_e = 1$, $e^2 = 1$, $h/2\pi = 1$, $4\pi\epsilon_0 = 1$) as

$$H_e = -\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \tag{7.33}$$

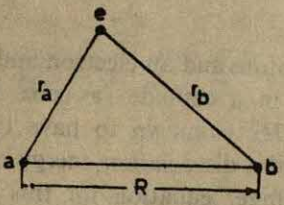

Fig. 7.4 *The coordinates for the hydrogen molecule ion*

Both a and b represent the hydrogen atoms, therefore

$$H_{aa} = H_{bb} \tag{7.34}$$

and the atomic orbitals $1s_a$ and $1s_b$ are separately normalised, so the integrals

$$\Delta_{aa} = \Delta_{bb} = 1 \tag{7.35}$$

The integral Δ_{ab} (or Δ_{ba}), called the overlap integral, is usually written as S. One may now write Eq. (7.30) as

$$(H_{aa} - E)^2 = (H_{ab} - SE)^2 \tag{7.36}$$

or

$$H_{aa} - E = \pm(H_{ab} - SE) \tag{7.37}$$

We have therefore two roots, viz.

$$E_1 = \frac{H_{aa} + H_{ab}}{1 + S} \tag{7.38}$$

$$E_2 = \frac{H_{aa} - H_{ab}}{1 - S} \tag{7.39}$$

Taking any one of the two secular equations, e.g.

$$C_1(H_{aa} - E) + C_2(H_{ab} - SE) = 0 \tag{7.40}$$

and introducing Eq. (7.37) into Eq. (7.40), one obtains for the root E_1

$$C_1 = C_2 \tag{7.41}$$

and for the root E_2

$$C_1 = -C_2 \tag{7.42}$$

That the coefficients C_1 and C_2 are equal in magnitude in H_2^+ also follows from the symmetry because both the atomic orbitals $1s_a$ and $1s_b$ are equivalent.

Therefore, the wavefunctions corresponding to the roots E_1 and E_2 are respectively

$$\psi_1 = C_1(1s_a + 1s_b) \tag{7.43}$$

$$\psi_2 = C_1(1s_a - 1s_b) \tag{7.44}$$

These orbitals are to be normalised. We have

$$\langle\psi_1 \mid \psi_1\rangle = C_1^2[\langle 1s_a \mid 1s_a \rangle + \langle 1s_b \mid 1s_b \rangle + 2\langle 1s_a \mid 1s_b \rangle]$$

or

$$C_1^2(2 + 2S) = 1$$

$$C_1 = \frac{1}{\sqrt{2 + 2S}} \tag{7.45}$$

Thus, the normalised MO, ψ_1 is given by

$$\psi_1 = \frac{1s_a + 1s_b}{\sqrt{2 + 2S}} \tag{7.46}$$

and by a similar procedure, the normalised MO, ψ_2 is given as

$$\psi_2 = \frac{1s_a - 1s_b}{\sqrt{2 - 2S}} \tag{7.47}$$

These two MOs, i.e., ψ_1 and ψ_2, are shown schematically along with their energies E_1 and E_2 in Fig. 7.5.

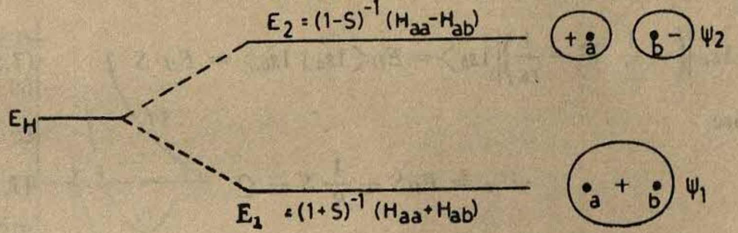
$E_2 = (1-S)^{-1}(H_{aa}-H_{ab})$
+ a
b −
ψ_2
E_H
a + b
ψ_1
$E_1 = (1+S)^{-1}(H_{aa}+H_{ab})$

Fig. 7.5 *Schematic representation of the molecular orbitals of H_2^+ where E_H is energy of the hydrogen atom in its ground state. Strictly, E_1 and E_2 are not symmetric about E_H for $S > 0$*

Now, we introduce Eq. (7.33) in H_{aa} which is defined in the set of Eqs. (7.31) and obtain

$$H_{aa} = \left\langle 1s_a \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_a} \right| 1s_a \right\rangle - \left\langle 1s_a \left| \frac{1}{r_b} \right| 1s_a \right\rangle + \left\langle 1s_a \left| \frac{1}{R} \right| 1s_a \right\rangle \tag{7.48}$$

Making use of the fact that the $1s$ function is a solution of the Schrödinger equation for the hydrogen atom, the first integral in Eq. (7.48) represents the energy of the hydrogen 1*s* atomic orbital and is denoted by E_H. The third integral is over the electronic coordinates while R is the nuclear coordinate and therefore Eq. (7.48) may be written as

$$H_{aa} = E_H + \frac{1}{R} - P \tag{7.49}$$

where

$$P = \left\langle 1s_a \left| \frac{1}{r_b} \right| 1s_a \right\rangle \tag{7.50}$$

Thus, the integral H_{aa} may be said to represent the energy of a hydrogen atom '*a*' perturbed by a proton '*b*' and is quite close to the energy of an unperturbed hydrogen atom except for very small values of R.

H_{ab} can be written similarly as

$$H_{ab} = \left\langle 1s_a \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_b} \right| 1s_b \right\rangle - \left\langle 1s_a \left| \frac{1}{r_a} \right| 1s_b \right\rangle + \frac{1}{R}\langle 1s_a \mid 1s_b \rangle \tag{7.51}$$

Since

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_b}\right) 1s_b = E_H \cdot 1s_b \tag{7.52}$$

multiplying both sides of Eq. (7.52) with $1s_a$ and integrating over all the electron space, one obtains

$$\left\langle 1s_a \left| \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_b}\right) \right| 1s_b \right\rangle = E_H \langle 1s_a \mid 1s_b \rangle = E_H \cdot S \tag{7.53}$$

Therefore,

$$H_{ab} = E_H S + \frac{1}{R} S - Q \tag{7.54}$$

where

$$Q = \left\langle 1s_a \left| \frac{1}{r_a} \right| 1s_b \right\rangle \tag{7.55}$$

The integral H_{ab} is generally called the resonance integral and represents the energy of the overlap density under the influence of the attractive field of both nuclei.

Entering expressions (7.49) and (7.54) into Eqs. (7.38) and (7.39) one obtains

$$E_1 = E_H + \frac{1}{R} - \frac{P + Q}{1 + S} \tag{7.56}$$

$$E_2 = E_H + \frac{1}{R} - \frac{P - Q}{1 - S} \tag{7.57}$$

The integrals P, Q and S are positive and it is seen that $E_1 < E_2$. Therefore, in the ground state of H_2^+, the electron occupies the MO ψ_1 and in its excited state, the MO ψ_2. The integrals P, Q and S can be evaluated in terms of R. Using the explicit form of the hydrogen 1s atomic orbital, i.e.,

$$1s_a = \frac{\exp(-r_a)}{\sqrt{\pi}} \tag{7.58}$$

the dependence of these integrals on the internuclear distance R is given by the following expressions

$$P = \frac{1}{R}\,[1 - (1 + R)\exp(-2R)] \tag{7.59}$$

$$Q = (1 + R)\exp(-R) \tag{7.60}$$

$$S = (1 + R + R^2/3)\exp(-R) \tag{7.61}$$

In Appendix 7 is shown the derivation of one of these expressions.

The potential energy curves for the two states of H_2^+ as a function of R can now be drawn ana are shown in Fig. 7.6. The calculated binding energy accounts for about 60% of the observed value and minimum occurs at $R = 2.49$ au (~1.32 Å). Although the agreement with the observed values is not very satisfactory, by allowing an electron to move in the neighbourhood of both nuclei, it has been possible to reproduce the characteristic of the true wavefunction essential to the formation of a stable molecule.

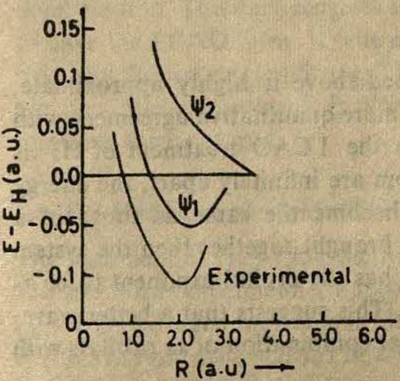

Fig. 7.6 *The potential energy curves for* H_2^+

The electron distributions in the two states ψ_1 and ψ_2 respectively are given by

$$\rho_1 = \psi_1^2 = (2 + 2S)^{-1}\,[1s_a^2 + 1s_b^2 + 2\cdot 1s_a\, 1s_b] \tag{7.62}$$

$$\rho_2 = \psi_2^2 = (2 - 2S)^{-1}\,[1s_a^2 + 1s_b^2 - 2\cdot 1s_a\, 1s_b] \tag{7.63}$$

At a point midway between the two protons (i.e. $r_a = r_b$) we have

$$1s_a = 1s_b$$

$$\psi_1 = \frac{2 \times 1s_a}{\sqrt{2 + 2S}}, \qquad \psi_2 = 0$$

$$\rho_1 = \frac{4 \times 1s_a^2}{2 + 2 \cdot S}, \rho_2 = 0$$

Thus, in the state ψ_1, more electron density is found between the nuclei than would be obtained from just the sum of the two separate atomic electron densities. The attraction between this accumulation of charge and the two protons leads to the stability of H_2^+ in state ψ_1. Therefore, ψ_1 is called the bonding molecular orbital. In state ψ_2, density at the centre of the bond is zero and is therefore less than the sum of the electron densities of the separate atoms. The MO ψ_2 is called the antibonding orbital. The densities along the internuclear axis are shown in Fig. 7.7.

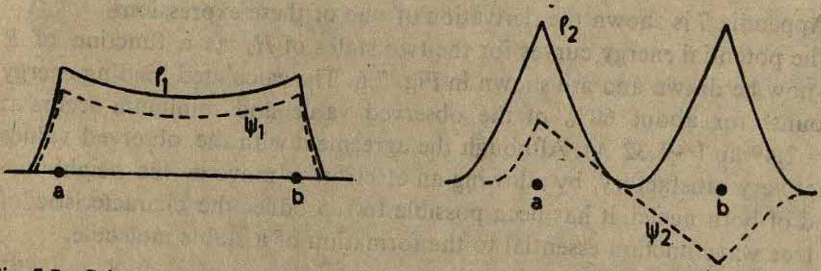

Fig. 7.7 *Schematic representation of the orbitals (dotted lines) and electron densities (solid lines) along the molecular axis in* H_2^+

Although the treatment of H_2^+ as described above is highly approximate, it gives qualitatively correct results. For a more quantitative agreement with the observed results, an improvement in the LCAO treatment of H_2^+ is necessary. If a proton and a hydrogen atom are infinitely apart, the energy and the wave function of such a system become the same as those of a hydrogen atom. If these two species are brought together then the system reduces to He^+, the $1s$ orbital of which has the orbital exponent twice as large as that of the $1s$ orbital of hydrogen. This suggests that a better wavefunction may be obtained by taking a linear combination of $1s$ orbitals with variable exponents,

$$1s_a = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp\left(-\alpha r_a\right)$$

$$1s_b = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp\left(-\alpha r_b\right) \tag{7.64}$$

where the value of α must be somewhere between one and two. Coulson[4] used these basis orbitals in the LCAO treatment of H_2^+ and found by the variation method that at the equilibrium bond length of 1.06 Å the value of α was 1.24, which gave a dissociation energy of 2.25 eV.

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[4] C.A. Coulson, *Trans. Faraday, Soc.*, 33, 1479, 1937.

Another improvement in the LCAO treatment of the H_2^+ has been suggested by Dickenson[5]. An electron in the vicinity of a nucleus a (or b) is not adequately described by the wavefunctions (7.64) because an atom in a molecule is different from an isolated atom which has always a spherically symmetrical electron density distribution. This spherical symmetry in the electron distribution is destroyed on the molecular formation and the atomic orbital is therefore polarised or distorted. In order to give effect to this Dickenson employed the following linear combination

$$[1s_a(\alpha) + C\,2p_a(\alpha')] + [1s_b(\alpha) + C\,2p_b(\alpha')] \tag{7.65}$$

where the $2p$-orbitals were oriented along the line joining the nuclei. The effect of adding $2p$-type orbital is to polarise the $1s$-orbital. The $1s$- and $2p$-functions were assigned to have separate orbital exponents, α and α' respectively. Here, C is an additional variation parameter. The energy was minimised for $R = 1.06$ Å with $\alpha = 1.247$, $\alpha' = 2.868$ and $C = 0.145$. The calculated dissociation energy was 2.65 eV.

James[6] has shown that extremely good dissociation energy of H_2^+ is obtained from a function

$$\psi = \exp\left[-\alpha(r_a + r_b)\,R\right]\left\{1 + C\cdot\frac{(r_a - r_b)^2}{R}\right\} \tag{7.66}$$

where α and C are the parameters chosen to minimise the energy function. The function in Eq. (7.66) discards the LCAO concept and leads to near-exact results. This fact seggests that the exact wavefunction does not have to have the LCAO form. It tells us that the atomic orbitals do not really have any "objective significance" in the language of McWeeny[7] (1979). They are used for convenience in dealing with molecules in terms of known solutions for its atoms.

7.6 The Hydrogen Molecule (The MO Method)

The treatment of H_2 within the framework of the molecular orbital theory and the Born-Oppenheimer approximation is essentially the same as that of H_2^+. The hydrogen molecule is described by an equation which considers the motion of two electrons in a field of two fixed protons separated by a distance, say R. The hamiltonian of such a system may be written (in atomic units) as

$$H_e = \tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R} \tag{7.67}$$

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[5] B.N. Dickenson, *J. Chem. Phys.*, **1**, 317, 1933.

[6] H.M. James, *J. Chem. Phys.*, **3**, 9, 1935.

[7] R. McWeeny, "*Coulson's Valence*," 3rd Edn., Chap. 4, Oxford University Press, 1979.

where 1 and 2 refer to electrons and a and b to protons (Fig. 7.8). Ignoring the nuclear repulsion term (i.e., $1/R$) which can be introduced later as this term is independent of the electronic coordinates, the hamiltonian of Eq. (7.67) can be written as

$$H_e = H'_e + \frac{1}{R} \tag{7.68}$$

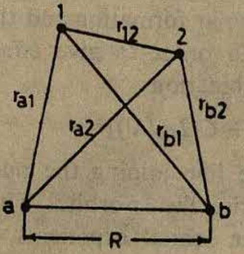

Fig. 7.8 *The coordinate system in a H_2 molecule*

where

$$H'_e = H^c(1) + H^c(2) + \frac{1}{r_{12}} \tag{7.69a}$$

and

$$H^c(1) = -\frac{\nabla_1^2}{2} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} \tag{7.69b}$$

$$H^c(2) = -\frac{\nabla_2^2}{2} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} \tag{7.69c}$$

If the electron repulsion is neglected, then the orbitals of H_2 are the solutions of the equations

$$H^c(i)\,\psi_k(i) = E_k\,\psi_k(i) \tag{7.70}$$

where i refers to either of the two electrons.

This is essentially the equation which was solved for H_2^+ in the earlier section within the framework of the LCAO approximation where the nuclear repulsion term was, however, retained. But the nuclear repulsion is independent of electronic coordinates, the total energy $E(R)$ of a diatomic system for a fixed nuclear framework is therefore related to the energy, E_{el} (where E_{el} is the energy without nuclear repulsion) by the equation

$$E = E_{el} + \frac{Z_a Z_b}{R} \tag{7.71}$$

where Z_a and Z_b are the nuclear charges of atoms a and b respectively. It makes no difference to electronic wavefunctions whether the $1/R$ term is retained in the hamiltonian or incorporated in the energy expression later. Thus, the normalised wavefunctions of Eq. (7.70) are

$$\psi_1 = \frac{1}{\sqrt{2(1+S)}}\,(1s_a + 1s_b) \tag{7.72}$$

$$\psi_2 = \frac{1}{\sqrt{2(1-S)}}\,(1s_a - 1s_b)$$

and their corresponding energies are

$$E_1 = (H^c_{aa} + H^c_{ab})\,(1 + S)^{-1}$$

$$E_2 = (H^c_{aa} - H^c_{ab})\,(1 - S)^{-1} \qquad (7.73)$$

where

$$H^c_{aa} = \langle\, 1s_a(i) \mid H^c(i) \mid 1s_a(i)\,\rangle$$

$$H^c_{ab} = \langle\, 1s_a(i) \mid H^c(i) \mid 1s_b(i)\,\rangle \qquad (7.74)$$

It now follows from Eqs. (7.49) and (7.54) that

$$H^c_{aa} = E_H - P$$

$$H^c_{ab} = E_H S - Q \qquad (7.75)$$

Both these integrals are negative because E_H is negative and therefore $E_1 < E_2$ in Eq. (7.73). In the ground state of the hydrogen molecule both the electrons occupy the orbital ψ_1, and the Slater determinantal form of the wavefunction for the ground state is given by

$$\Psi_0 = \frac{1}{\sqrt{2}} \mid \psi_1(1)\, \overline{\psi}_1(2) \mid \qquad (7.76)$$

Let us now evaluate the ground state energy. The electronic energy is given by

$$E_{el} = \left\langle \Psi_0 \left| \left(H^c(1) + H^c(2) + \frac{1}{r_{12}} \right) \right| \Psi_0 \right\rangle \qquad (7.77)$$

This integral is over the space as well as spin coordinates of both electrons. The procedure of obtaining more explicit form of this integral is exactly the same as it was followed in the calculation of the ground state energy of the helium atom (see Eq. (6.30)].

Thus one obtains

$$E_{el} = 2E_1 + J_{11} \qquad (7.78)$$

where

$$J_{11} = \left\langle \psi_1(1)\psi_1(1) \left| \frac{1}{r_{12}} \right| \psi_1(2)\psi_1(2) \right\rangle$$

$$= \iint \psi_1^2(1) \left| \frac{1}{r_{12}} \right| \psi_1^2(2)\,\partial\tau_1 \partial\tau_2 \qquad (7.79)$$

Using the form of ψ_1 given by Eq. (7.72), J_{11} may be expressed in terms of the integrals over the atomic orbitals.

$$J_{11} = \frac{1}{4(1+S)^2}[2\langle aa \mid aa\rangle + 2\langle aa \mid bb\rangle$$

$$+ 8\langle aa \mid ab\rangle + 4\langle ab \mid ab\rangle] \qquad (7.80)$$

where

$$\langle aa \mid aa\rangle = \iint 1s_a(1)1s_a(1) \left| \frac{1}{r_{12}} \right| 1s_a(2)1s_a(2)\, d\tau_1\, d\tau_2 \qquad (7.81)$$

is the one-centre integral of the type encountered in the calculation of the energy of the helium atom,

$$\langle aa \mid bb \rangle = \iint 1s_a(1)1s_a(1)\left|\frac{1}{r_{12}}\right| 1s_b(2)1s_b(2)\, d\tau_1\, d\tau_2 \tag{7.82}$$

is the two-centre coulomb integral,

$$\langle aa \mid ab \rangle = \iint 1s_a(1)1s_a(1)\left|\frac{1}{r_{12}}\right| 1s_a(2)1s_b(2)\, d\tau_1\, d\tau_2 \tag{7.83}$$

called the two-centre hybrid integral, and

$$\langle ab \mid ab \rangle = \iint 1s_a(1)1s_b(1)\left|\frac{1}{r_{12}}\right| 1s_a(2)1s_b(2)\, d\tau_1\, d\tau_2 \tag{7.84}$$

called the two-centre exchange integral. All these integrals except the first one depend on R, the distance between the two nuclear centres. For analytic expressions of these integrals the reader is referred to the tables given by Kotani et al.[8]

Inserting Eqs. (7.73) and (7.75) in Eq. (7.78) and incorporating the nuclear repulsion term, the ground state energy $E_0(R)$ of the hydrogen molecule may be written as

$$E_0(R) = 2E_H - \frac{2(P+Q)}{1+S} + J_{11} + \frac{1}{R} \tag{7.85}$$

The molecular energy is calculated as a function of internuclear distance and plotted in Fig. 7.9: curve (a). The minimum value of E_0 is found for $R = 0.84$ Å. The observed equilibrium bond length in H_2 is 0.74 Å. The calculated bond energy is 2.68 eV while the observed value is 4.75 eV. Thus, the simple molecular orbital theory accounts for only 56% of the observed bond energy. Furthermore, when R becomes infinitely large, the energy E_0 of Eq. (7.85) does not converge toward the value of $2E_H$. This may be evident from the following argument. At $R = \infty$, each of the integrals, P, Q and S becomes zero, and all but the first integral vanishes in Eq. (7.80). Therefore from Eqs. (7.80) and (7.85) we get

$$E_0(\infty) = 2E_H + 1/2 \langle aa \mid aa \rangle \tag{7.86}$$

This shows that the simple molecular orbital picture does not describe the molecular dissociation correctly. The reason for this failure can be found from the form of the molecular wavefunction, Ψ_0 of Eq. (7.76) which may be written in the following form

$$\Psi_0 = \psi_1(1)\psi_1(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{7.87}$$

Ignoring the spin part of the wavefunction, one may write, after inserting the form of ψ_1 provided by Eq. (7.72)

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[8] Kotani et al., *Tables of Molecular Integrals*, Muruzen and Co., Tokyo, 1955.

$$\Psi_0 = \frac{1}{\sqrt{2(1+S)}}[1s_a(1)1s_a(2) + 1s_b(1)1s_b(2) + 1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)] \tag{7.88}$$

The first and second terms correspond to the situation in which both electrons are associated with the same portion, i.e., $H_a^- - H_b^+$ and $H_b^- - H_a^+$. Since the ionisation potential of a hydrogen atom is high while the electron affinity is low, the reaction $2H \rightarrow H^+ + H^-$ ought to be highly endothermic and, therefore, the occurrence of the ionic structures is likely to be very rare. On the other hand, the third and fourth terms in Eq. (7.88) correspond to the situation in which electrons are shared equally by both the protons and therefore they correspond to the covalent structure of H_2. If we define Ψ_{cov} and Ψ_{ion} as

$$\Psi_{\text{cov}} = \frac{1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)}{\sqrt{2(1+S^2)}} \tag{7.89}$$

$$\Psi_{\text{ion}} = \frac{1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)}{\sqrt{2(1+S^2)}} \tag{7.90}$$

then Ψ_0 can be written as

$$\Psi_0 = \frac{\sqrt{2(1+S^2)}}{2(1+S)}(\Psi_{\text{cov}} + \Psi_{\text{ion}}) \tag{7.91}$$

It is easily seen that the molecular-orbital approach gives equal weight to the ionic and covalent structures. This is highly unreasonable for the hydrogen molecule and, therefore, responsible for the poor agreement between the calculated and observed results.

This shortcoming of the MO wavefunction can also be discussed from another point of view as follows. The MO wavefunction ψ_0 as given by Eq. (7.87) takes into account the spin correlation. But an α-electron and β-electron may come as close together as they wish. Hence the relative probability of finding the electron 1 in different regions of space is independent of the position of electron 2. If an electron is found at a point in space, the probability of the second electron coming close to the first electron should be very small on account of the Coulomb repulsion. In other words, the positions of electrons in a many-electron system should be correlated. A true wavefunction must take into account this charge-correlation of electrons. While Ψ_{cov} describes a very strong charge-correlation because in this wavefunction when one electron is found near the nucleus '*a*' the other electron is associated with the nucleus '*b*' Ψ_{ion} disregards this correlation and in the limit of equal contributions of Ψ_{cov} and Ψ_{ion} [Eq. (7.91)] the charge-correlation is ignored completely.

7.7 The Valence-Bond (VB) Method

The first quantum mechanical theory of chemical bond was given by Heitler and London in 1927.[9] This was later developed by Pauling and others into a more comprehensive theory of bonding. This approach and its applications were reviewed by Pauling[10] in 1960 and is now known as valence bond theory. Here we outline the approach originally put forward by Heitler and London for treatment of H_2.

If a system consists of two atoms *a* and *b* then its total wavefunction will be the product of the wavefunctions of the components. Let $1s_a$ and $1s_b$ be the 1*s*-orbitals of the two hydrogen atoms in their ground state. If an electron labelled as '1' is around the nucleus '*a*' and the electron labelled as '2' near the nucleus '*b*' then the wavefunction of the composite system be given as $1s_a(1)1s_b(2)$. When the two atoms are very near each other, say about 1 Å apart, it is difficult to say that electron '1' is around the nucleus '*a*' and the electron '2' around the nucleus '*b*'. In fact, electrons are identical particles and there is no way to distinguish the wavefunction $1s_a(1)1s_b(2)$ from $1s_a(2)1s_b(1)$. The essential feature of the VB description of H_2 was to choose the two-electron wavefunction as

$$\Psi(1, 2) = C_1\Phi_1 + C_2\Phi_2 \tag{7.92}$$

where

$$\left.\begin{aligned} \Phi_1 &= 1s_a(1)1s_b(2) \\ \Phi_2 &= 1s_a(2)1s_b(1) \end{aligned}\right\} \tag{7.92a}$$

Since both the atoms are the hydrogen atoms, by symmetry one can tell that

$$C_1^2 = C_2^2 \quad \text{or} \quad C_1 = \pm C_2$$

The energy of the system is given by

$$E = \frac{\langle \Psi(1, 2) \mid H_e \mid \Psi(1, 2) \rangle}{\langle \Psi(1, 2) \mid \Psi(1, 2) \rangle} \tag{7.93}$$

Application of the variation principle to Eq. (7.93) leads to the following secular equations

$$\left.\begin{aligned} C_1(H_{11} - E) + C_2(H_{12} - S^2E) &= 0 \\ C_1(H_{21} - S^2E) + C_2(H_{22} - E) &= 0 \end{aligned}\right\} \tag{7.94}$$

where

$$\begin{aligned} H_{11} &= \langle \Phi_1 \mid H_e \mid \Phi_1 \rangle \\ H_{22} &= \langle \Phi_2 \mid H_e \mid \Phi_2 \rangle \\ H_{12} = H_{21} &= \langle \Phi_1 \mid H_e \mid \Phi_2 \rangle \\ S^2 &= \langle \Phi_1 \mid \Phi_2 \rangle \end{aligned}$$

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[9] H. Heitler and F. London, *Z. Phys.*, **44**, 455, 1927.

[10] L. Pauling, *Nature of the Chemical Bond*, 3rd Edn., Cornell University Press, New York, 1960.

and the hamiltonian H_e is given by Eq. (7.67) for H_2. Since $H_{11} = H_{22}$ the secular determinant of Eq. (7.94) leads to

$$(H_{11} - E)^2 = (H_{12} - S^2E)^2$$

$$H_{11} - E = \pm(H_{12} - S^2E)$$

or

$$E_+ = \frac{H_{11} + H_{12}}{1 + S^2}, \quad E_- = \frac{H_{11} - H_{12}}{1 - S^2} \tag{7.95}$$

Thus we get two energy levels for H_2. Substitution of these roots into Eq. (7.94) leads to two functions. The wavefunction whose energy is E_+ is given by

$$\Psi_+ = C_1[\Phi_1 + \Phi_2] \tag{7.96}$$

and the function whose energy is E_- is given by

$$\Psi_- = C_1[\Phi_1 - \Phi_2] \tag{7.97}$$

Normalisation gives

$$\int \Psi_+^2 \, d\tau_1 \, d\tau_2 = 1$$

$$C_1^2\left[\int \Phi_1^2 \, d\tau_1 \, d\tau_2 + \int \Phi_2^2 \, d\tau_1 \, d\tau_2 + 2\int \Phi_1\Phi_2 \, d\tau_1 \, d\tau_2\right] = 1$$

$$C_1^2\left[\int 1s_a^2(1) \, d\tau_1 \int 1s_b^2(2) \, d\tau_2 + \int 1s_a^2(2) \, d\tau_2 \int 1s_b^2(1) \, d\tau_1\right.$$

$$\left. + 2\int 1s_a(1)1s_b(1) \, d\tau_1 \int 1s_b(2)1s_a(2) \, d\tau_2\right] = 1$$

$$C_1^2[2 + 2S^2] = 1$$

$$C_1^2 = \frac{1}{2 + 2S^2} \quad \text{or} \quad C_1 = \frac{1}{\sqrt{2 + 2S^2}} \tag{7.98}$$

The normalised wavefunctions of H_2 are therefore given by

$$\Psi_+ = \frac{\Phi_1 + \Phi_2}{\sqrt{2 + 2S^2}} \tag{7.99}$$

$$\Psi_- = \frac{\Phi_1 - \Phi_2}{\sqrt{2 - 2S^2}} \tag{7.100}$$

We shall now evaluate the integrals H_{11} and H_{12}. If we split the electronic hamiltonian according to Eq. (7.68) and Eqs (7.69), we obtain

$$\begin{aligned} H_{11} &= \left\langle 1s_a(1)1s_b(2) \left| \left(H^c(1) + H^c(2) + \frac{1}{r_{12}}\right) \right| 1s_a(1)1s_b(2) \right\rangle \\ &= \langle 1s_a(1) \mid H^c(1) \mid 1s_a(1) \rangle + \langle 1s_b(2) \mid H^c(2) \mid 1s_b(2) \rangle \\ &\quad + \langle aa \mid bb \rangle \end{aligned} \tag{7.101}$$

The electron repulsion integral $\langle aa \mid bb \rangle$ is defined by Eq. (7.82) earlier.

$$\begin{aligned}&\langle 1s_a(1) \mid H^c(1) \mid 1s_a(1) \rangle \\ &= \left\langle 1s_a(1) \left| -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} \right| 1s_a(1) \right\rangle - \left\langle 1s_a(1) \left| \frac{1}{r_{b1}} \right| 1s_a(1) \right\rangle \\ &= E_H - P \qquad (7.102)\end{aligned}$$

P is defined by Eq. (7.50).
The expression for $\langle 1s_b(2) \mid H^c(2) \mid 1s_b(2) \rangle$ is same as in Eq. (7.102) because $1s_a$ and $1s_b$ refer to two hydrogen atoms. One may write now

$$H_{11} = 2E_H - 2P + \langle aa \mid bb \rangle \qquad (7.103)$$

Similarly, we proceed for H_{12} as follows.

$$\begin{aligned}H_{12} &= \left\langle 1s_a(1)1s_b(2) \left| \left(H^c(1) + H^c(2) + \frac{1}{r_{12}}\right) \right| 1s_b(1)1s_a(2) \right\rangle \\ &= \langle 1s_a(1) \mid H^c(1) \mid 1s_a(1) \rangle S + \langle 1s_b(2) \mid H^c(2) \mid 1s_a(2) \rangle S \\ &\quad + \langle ab \mid ab \rangle \qquad (7.104)\end{aligned}$$

The two-centre exchange integral $\langle ab \mid ab \rangle$ is defined in Eq. (7.84).

$$\begin{aligned}\langle 1s_a(1) \mid H^c(1) \mid 1s_b(1) \rangle &= \left\langle 1s_a(1) \left| -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{b1}} \right| 1s_b(1) \right. \\ &\quad - \left\langle 1s_a(1) \left| \frac{1}{r_{a1}} \right| 1s_b(1) \right\rangle \\ &= E_H S - Q \qquad (7.105)\end{aligned}$$

Q is defined by Eq. (7.55). The expression for the second term of Eq. (7.104) is same as in Eq. (7.105).

$$H_{12} = 2E_H S^2 - 2SQ + \langle ab \mid ab \rangle \qquad (7.106)$$

Since $E_H = -13.6$ eV and P and Q are positive and increase with decrease of R [see Eq. (7.59) and (7.60)], Eq. (7.103) and (7.106) show that both H_{11} and H_{12} are the negative quantities. This implies $E_+ < E_-$. In other words, the ground state wavefunction of H$_2$ is given by Ψ_+ of Eq. (7.99). The total ground state energy, E_0 of H_2 is given as

$$\begin{aligned}E_0(R) &= E_+ + \frac{1}{R} = \frac{H_{11} + H_{12}}{1 + S^2} + \frac{1}{R} \\ &= 2E_H - 2\frac{P + QS}{1 + S^2} + \frac{1}{1 + S^2}[\langle aa \mid bb \rangle + \langle ab \mid ab \rangle] + \frac{1}{R} \qquad (7.107)\end{aligned}$$

All the integrals in Eq. (7.107) decrease with increase of R and vanish at $R = \infty$. Therefore the total energy of H$_2$ reduces to $2E_H$ when the atoms are infinitely separated. Thus, the VB picture gives a proper description of the molecular dissociation. Heitler and London calculated the total energy $E_+ + 1/R$ as a function of R and obtained the dissociation energy of 3.16 eV and the equilibrium bond length of 0.87 Å (1.67 au). [See Fig. (7.9), curve b].

Considering the simple type of approach this result is superior to the simple MO picture discussed earlier. The wavefunction Ψ_+ is same as the function Ψ_{cov} of Eq. (7.89). The bonding in the VB picture of H_2 arises from the presence of H_{12} and the wavefunction Ψ_+ now tells us what the electron sharing Lewis meant in 1916. If we had used the term Φ_1 alone i.e., $1s_a(1)\,1s_b(2)$, in the wavefunction Φ_+ and then determined the energy as a function R we would have obtained the binding energy of only 0.25 eV. Thus, the strong bonding in H_2 is due to the exchange of electrons between the two nuclei and the integral H_{12} may be called the exchange or resonance integral. It should be noted that this concept of exchange arises from the use of atomic orbitals while the exchange is not a genuine phenomenon (See Sec. 7.9).

Since the ground state wavefunction Ψ_+ is symmetric with respect to the interchange of the positional coordinates of the two electrons, the Pauli principle requires that this function must be combined with the antisymmetric spin function, i.e.,

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

to obtain a singlet state for H_2. On the other hand, the excited state wavefunction Ψ_- is antisymmetric with respect to interchange of the positional coordinates. The Pauli principle requires that Ψ_- be associated with the symmetric spin functions. We shall discuss the symmetric spin functions in Sec. 7.10. Here, we mention that Ψ_- refers to the lowest triplet state of H_2 and its total energy, E_0' is given by

$$\begin{aligned} E_0'(R) &= E_- + \frac{1}{R} = \frac{H_{11} - H_{12}}{1 - S^2} + \frac{1}{R} \\ &= 2E_H - 2\,\frac{(P - QS)}{1 - S^2} + \frac{1}{1 - S^2}[\langle aa \mid bb \rangle - \langle ab \mid ab \rangle] + \frac{1}{R} \end{aligned} \tag{7.108}$$

The triplet energy curve is shown in Fig. 7.9(c) where we see that while the ground singlet state is stable, the lowest triplet state is unstable and does not represent a stable excited state of H_2. Hydrogen molecules excited to higher triplet states can make transitions to this unstable state and then dissociate spontaneously into hydrogen atoms with large kinetic energies. The spectrum of ultra-violet light emitted in this process is continuous and from a careful analysis of the intensity distribution of this continuous spectrum one can determine the potential energy curve for this unstable state which is shown in Fig. 7.9(d) as the experimental curve for the triplet state.

7.8 Charge Distribution in Molecular Hydrogen

If the total wavefunction of a many-electron system is given by $\Psi(1,2,3,\ldots,n)$ then $\Psi^2\,d\tau_1\,d\tau_2\ldots d\tau_n$ gives the probability of finding electron '1' in volume of space $d\tau_1$, electron '2' in $d\tau_2$, etc. If, however, we are interested in electron '1' then the density function $\rho(1)$ for the electron '1' will be so

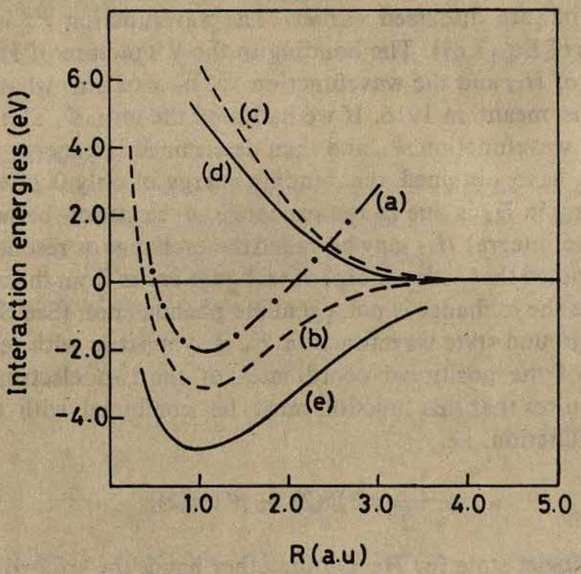

Fig. 7.9 *Interaction energies vs. R(au) for H_2. Interaction energy is defined as* $(E_0 - 2E_H)$ *and is given in* $eV[1\ eV = 0.0367\ au]$; *(a) the energy curve of* $\psi_0(MO)$, *(b) the energy curve for* $\psi_+(VB)$, *(c) the energy curve for* $\psi_-(VB)$, *(d) the experimental energy curve for the triplet state, (e) the experimental energy curve for the ground singlet state*

defined that $\rho(1)\, d\tau_1$ represents the sum of all the probabilities corresponding to electron 1 in $d\tau_1$ while all other electrons 2, 3, etc., will be found in all possible regions of space.

The hydrogen molecule has two electrons and its ground state wavefunction $\Psi(1, 2)$ is given by either Eq. (7.76) according to the MO theory or by Eq. (7.99) according to the VB theory. So $\rho(1)\, d\tau_1$ is given by

$$\rho(1)\, d\tau_1 = \left[\int \Psi_0^2(1, 2)\, d\tau_2\right] d\tau_1 \tag{7.109}$$

Following Eq. (7.76), $\Psi_0(1, 2)$ is given by

$$\Psi_0(1,2) = \frac{1}{\sqrt{2}}[\psi_1(1)\bar{\psi}_1(2) - \psi_1(2)\bar{\psi}_1(1)] \tag{7.110}$$

Substituting Eq. (7.110) in Eq. (7.109) we have

$$\begin{aligned}\rho(1) &= \tfrac{1}{2}\left[\psi_1^2(1)\int \bar{\psi}_1^2(2)\, d\tau_2 + \bar{\psi}_1^2(1)\int \psi_1^2(2)\, d\tau_2\right.\\ &\qquad \left. -2\psi_1(1)\bar{\psi}_1(1)\int \bar{\psi}_1(2)\psi_1(2)\, d\tau\right]\\ &= \frac{1}{2}\left[\psi_1^2(1) + \bar{\psi}_1^2(1)\right]\end{aligned} \tag{7.111}$$

The integral $\int \psi_1(2)\Psi_1(2)\, d\tau_2$ is over the spin-orbit space and vanishes due to orthogonality of the spin functions [see Sec. 7.10]. After substitution of Eq. (7.72) for ψ_1, the density function $\rho(1)$ (spinless) is given by

$$\rho(1) = \psi_1^2(1) = \frac{1s_a^2(1) + 1s_b^2(1) + 2\times 1s_a(1)1s_b(1)}{2(1+S)} \tag{7.112}$$

Since electrons 1 and 2 are indistinguishable $\rho(2)$ for the second electron must have the same value. The total one-electron density function is

$$\rho = \rho(1) + \rho(2) = 2\rho(1) \tag{7.113}$$

It is this density which is observed in x-ray experiments. One may write

$$\rho = 2\rho(1) = \frac{2}{2(1+S)}\,[1s_a^2 + 1s_b^2 + 2\times 1s_a\cdot 1s_b] \tag{7.114}$$

If we integrate ρ over all space for electron 1, we have

$$\begin{aligned}\int \rho\, d\tau_1 &= \frac{2}{2+2S}\left[\int 1s_a^2\, d\tau_1 + \int 1s_b^2\, d\tau_1 + 2\int 1s_a\cdot 1s_b\, d\tau_1\right]\\ &= 2\end{aligned} \tag{7.115}$$

We get the total number of electrons, i.e. 2. We can split $\int \rho\, d\tau_1$ according to Eq. (7.115) as

$$\int \rho\, d\tau_1 = \frac{1}{1+S} + \frac{1}{1+S} + \frac{2S}{1+S} = 2 \tag{7.116}$$

This means that, of the two electrons in H_2, $1/1+S$ electrons are associated with each hydrogen atom and $2S/1+S$ electrons remain in the internuclear region of the bond. These numbers are called electron populations by Mulliken.[11]

If we substitute Eq. (7.99) for $\Psi(1, 2)$, then the spinless density function $\rho(1)$ will be given by

$$\begin{aligned}\rho(1) &= \int \Psi_+^2\, d\tau_2\\ &= \frac{1}{2(1+S^2)}\left[\int \Phi_1^2\, d\tau_2 + \int \Phi_2^2\, d\tau_2 + 2\int \Phi_1\Phi_2\, d\tau_2\right]\end{aligned}$$

which leads to

$$\rho(1) = \frac{1s_a^2(1) + 1s_b^2(1) + 2\times 1s_a(1)1s_b(1)S}{2(1+S^2)}$$

So the total electron density is

$$\begin{aligned}\rho &= \rho(1) + \rho(2) = 2\rho(1)\\ &= \frac{1}{1+S^2}[1s_a^2 + 1s_b^2 + 2\times 1s_a\cdot 1s_b\cdot S]\end{aligned} \tag{7.117}$$

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[11] R.S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1997, (1955).

Thus, according to thc VB theory, $1/(1 + S^2)$ electrons are associated with each hydrogen atom while $2S/(1 + S^2)$ electrons are found in the internuclear region.

The MO and VB theories give nearly the same picture of covalent bonding which shifts the electron densities from atoms to the internuclear region. Since $0 < S < 1$ the MO theory leads to a slightly bigger build-up of density in the overlap region than the VB theory.

7.9 Beyond the Simple MO and VB Approximations

There are various kinds of refinements that different people have introduced to obtain better wavefunctions and energies for H_2. We shall discuss only a few.

The first refinement of the Heitler-London approach of H_2 was suggested by Wang in 1928.[12] The atomic function $1s$ of the hydrogen atom corresponds to unit nuclear charge. But when an electron sees the field of two protons of approximately 1 Å apart it feels an enhanced attraction. This would mean that the effective nuclear charge Z' is greater than one. Indeed, the two H-atoms coalesce to produce the united atom He, the appropriate value of Z' is 1.69 (see Sec. 6.2). Wang tried with $1s$ orbitals

$$1s_a(1) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp(-\alpha r_{a1})$$

$$1s_b(2) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp(-\alpha r_{b1})$$

where the effective charge α is an adjustable factor. With these orbitals he treated H_2 according to the Heitler-London procedure and varied α. At each value of R, α is varied to minimise the energy by the variation method. Wang obtained for H_2 the binding energy of 3.78 eV, and $\alpha = 1.166$; a considerable improvement over the previous value of 3.14 eV. Another good point of Wang's treatment is that his wavefunctions satisfy the virial theorem which is not obeyed by the Heitler-London functions at the minimum point of the adiabatic potential energy curve.

The second refinement in the VB approach is to argue that when two atoms are near each other (say $\sim$ 1 Å apart) there is a possibility that both electrons may be found around one nucleus. A suitable wavefunction would be $1s_a(1)\ 1s_a(2)$ or $1s_b(1)\ 1s_b(2)$. Since both are equally probable so far as H_2 is concerned, we must take the following trial VB function

$$\begin{aligned}\Psi &= [1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)] + \lambda[1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)] \\ &= \Psi_{\text{cov}} + \lambda\Psi_{\text{ion}} \qquad (7.118)\end{aligned}$$

where Ψ_{cov} denotes the original Heitler-London function and Ψ_{ion} denotes the ionic term which we come across in Eq. (7.90). The wavefunction in Eq. (7.118) is not normalised. We have now essentially two adjustable parameters α and λ. The best function is obtained by varying them so as to minimise the total electronic energy. Weinbaum[13] found that at the equilibrium position $\lambda \approx 1/6$, $\alpha = 1.19$ and the binding energy was increased from Wang's value of 3.78 eV to 4.02 eV. Both Wang's and Weinbaum's results led to $\alpha > 1$ at the equilibrium bond length.

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[12] S. Wang. *Phys. Rev.*, **31**, 579 (1928).

We have already shown the ionic and covalent contributions in the simple MO picture of H_2 and found that they contribute equally to bonding in H_2. This is unrealistic and is responsible for the poor description of bonding in H_2 and the improper description of the molecular dissociation. Coulson[4] tried to improve the MO description of H_2 by varying the orbital exponent of the atomic orbitals as in the case of H_2^+ and obtained better binding energy. However, the improper description of the dissociation of H_2 can be remedied by taking a proper account of the charge-correlation through configuration interaction (see Sec. 6.5). In molecules, besides the angular and radial (or in-out) correlations, the horizontal correlation is important.

The ground state of H_2 is built up from the double occupation of the MO ψ_1 [Eq. (7.72)] which is symmetric with respect to inversion at the centre of the bond. We can construct an excited state of the same symmetry as the ground state by promoting both electrons into the MO ψ_2 [Eq. (7.72)], which is antisymmetric. Since there are two electrons in ψ_2, the resulting wavefunction

$$\Psi_2 = \frac{1}{\sqrt{2}} \mid \psi_2(1)\bar{\psi}_2(2) \mid \tag{7.119}$$

is again symmetric. The MO ψ_2 possesses a node at the midpoint of the bond [see Fig. 7.7 for ψ_2] and its purpose is to keep the electrons at opposite ends of the molecule. The effect of the configuration Ψ_2 is to remove charge density from the internuclear region and to concentrate it in the vicinity of the nuclei. This is known as the left-right (or horizontal) correlation of the electronic motions, which can be effected by mixing Ψ_0 with Ψ_2. It is this correlation which is important at large R and responsible for description of molecular dissociation.

Although the MOs ψ_1 and ψ_2 are mutually orthogonal the matrix element of $1/r_{12}$ linking Ψ_0 of Eq. (7.76) and Ψ_2 of Eq. (7.119) does not vanish so that these two configurations interact. Since Ψ_2 can be shown to have the form

$$\Psi_2 = \frac{\sqrt{2(1 + S^2)}}{2(1 + S)} (\Psi_{\text{ion}} - \Psi_{\text{cov}}) \tag{7.120}$$

an appropriate linear combination of Ψ_0 and Ψ_2 can give a proper balance between the ionic and the covalent contributions in the MO picture of H_2. We therefore consider a linear combination of the two configurations.

$$\theta_G = C(R)\Psi_0 + d(R)\Psi_2 \tag{7.121}$$

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[13] S. Weinbaum, *J. Chem. Phys.*, 1, 593, 1933.

where Θ_G is the improved wavefunction for the ground state, c and d are the variational parameters which are functions of R. One can improve the wavefunction still further by adding additional configurations as long as they have the correct symmetries. For a function of Eq. 7.121 the variation principle leads to the following 2×2 secular determinant

$$\begin{vmatrix} H_{00} - E & H_{02} \\ H_{02} & H_{22} - E \end{vmatrix} = 0 \tag{7.122}$$

where
$$\left.\begin{aligned} H_{00} &= \langle \Psi_0 \mid H_e \mid \Psi_0 \rangle = 2E_1 + J_{11} \text{ [see Eq. 7.8]} \\ H_{22} &= \langle \Psi_2 \mid H_e \mid \Psi_2 \rangle = 2E_2 + J_{22} \\ H_{02} &= \langle \Psi_0 \mid H_e \mid \Psi_2 \rangle \\ &= \iint \Psi_1(1)\Psi_2(1) \left| \frac{1}{r_{12}} \right| \Psi_1(2)\Psi_2(2)\, d\tau_1\, d\tau_2 \\ &= K_{12} \end{aligned}\right\} \tag{7.123}$$

The two roots of Eq. 7.122 are given by

$$E = \frac{(H_{00} + H_{22}) \pm \sqrt{(H_{00} - H_{22})^2 + 4K_{12}^2}}{2} \tag{7.124}$$

The lower root (which is obviously the one with a negative sign before the square root) corresponds to the energy of the ground state. The problem of determining the energy is again reduced to the problem of calculating the electron repulsion integrals J_{11}, J_{22} and K_{12} and the integrals E_1 and E_2. It can be easily shown after substituting Eq. (7.72) for ψ_1 and ψ_2 in Eq. 7.123 that at $R = \infty$.

$$\begin{aligned} J_{11} &= J_{22} = 1/2 \langle aa \mid aa \rangle \\ H_{00} &= H_{22} = 2E_H + 1/2 \langle aa \mid aa \rangle \\ K_{12} &= 1/2 \langle aa \mid aa \rangle \end{aligned} \tag{7.125}$$

Therefore, the ground state energy of H_2 following Eq. 7.124 converges toward the limiting value of $2E_H$ as $R \to \infty$. In Fig. 7.10 are shown the potential energy curves of the ground state of H_2 described by the simple MO function and the improved funcion Θ_G.

Although the simple VB picture is superior to the simple MO picture the MO calculations are much easier and easily extendable to polyatomic molecules. Excited states are quite awkward to deal with by the VB treatment. Electronic spectra are easily interpreted in terms of single-electron transitions between two MOs. We shall deal with the excited state of H_2 according to the MO theory in the next section. It is important to mention that both the VB and MO treatments show that better energies are obtained if the orbital exponent, α, of the atomic orbitals are varied to minimise the energy by the variation method. At the equilibrium bond lengths of H_2 and H_2^+, $\alpha > 1$. Figure 7.11 shows the variation of the wavefunction of the $1s$ orbitals of a hydrogen atom from the nucleus for $\alpha = 1$ and $\alpha > 1$. For

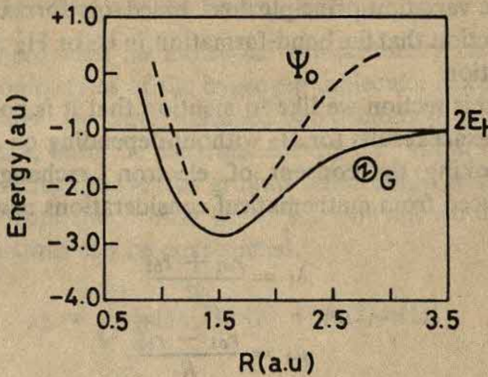

Fig. 7.10 *Potential energy curves of H_2 using Ψ_0 and Θ_G.*

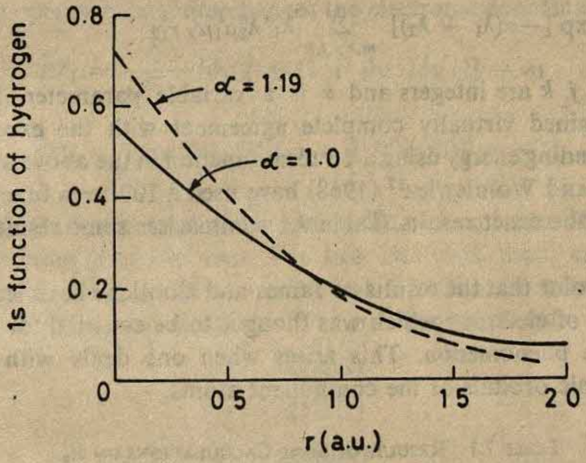

Fig. 7.11 *Variation of wavefunctions of 1s atomic orbitals of hydrogen for $\alpha = 1$, $\alpha = 1.19$.*

$\alpha > 1$, the function decays more rapidly away from the nucleus indicating that the densities are more compact. This means that bond-formation from atoms is accompanied by orbital contraction. This question was examined by Ruedenberg[14] who found by studying the variation of the electronic kinetic energy in H_2^+ that orbitals contract or more correctly the densities contract on bond-formation. This contraction is neither an artifact of the variation principle which is used to optimise the orbital exponent nor a sort of gimmick because of the use of the atomic orbitals in the LCAO or VB scheme. Kutzzelnigg and Schwartz[15] have demonstrated using a criterion independent of the variation principle and based on formal properties of the exact wavefunction that the bond-formation in H_2 or H_2^+ is accompanied by charge contraction.

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[14] K. Ruedenberg, *Localisation and Delocalisation in Quantum Chemistry*, Edited by O. Chalvet et al. (Reidel, Dordrecht, 1975), Vol. 1, Page 223.

[15] W. Kutzzelnigg and W.H.E. Schwartz, *Phys. Rev. A*, **26**, 2361, 1982.

Before leaving this section we like to mention that it is possible to obtain very accurate or exact results for H_2 without depending on atomic orbitals and without invoking the concept of electron exchange. James and Coolidge[16] introduced from mathematical considerations new coordinates

$$\lambda_1 = \frac{r_{a1} + r_{b1}}{R}$$

and

$$\mu_1 = \frac{r_{a1} - r_{b1}}{R}$$

for electron 1 and similarly for electron 2 and r_{12} for the interelectronic distance. They used as variation function a mixture of terms such as

$$\exp\left[-\alpha(\lambda_1 + \lambda_2)\right] \sum_{m,n,i,j,k} \lambda_1^m \lambda_2^n \mu_1^i \mu_2^j r_{12}^k \qquad (7.126)$$

where m, n, i, j, k are integers and α is a variable parameter. James and Coolidge obtained virtually complete agreement with the experimentally determined binding energy using a 13-term function in the above summation. Later, Kolos and Wolniewiez[17] (1968) have used a 100-term function for H_2 and obtained the exact results. Table 7.1 summarises some results of calculations for H_2.

The main point that the results of James and Coolidge have led to is that the exchange of electrons which was thought to be essential for bonding is not a genuine phenomenon. This arises when one deals with molecules using the atomic orbitals of the component atoms.

Table 7.1 Results of Some Calculations on H_2

Type of wavefunction	*Bond energy* (eV)	Re (Å)
Heitler-London	3.14	0.87
Wang	3.78	0.744
Weinbaum	4.02	0.74
Molecular orbital (Simple)	2.68	0.84
Molecular orbital with optimised orbital exponent (Coulson)	3.49	0.730
James-Coolidge [13-term function]	4.72	0.740
Kolos-Wolniewiez [100-term function]	4.746	0.741
Experiment	4.746	0.741

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[16] H.M. James and A.L. Coolidge, *J. Chem. Phys.*, 1, 825, 1933.

[17] W. Kolos and L. Wolniewiez, *J. Chem. Phys.*, 49, 404, 1968.

7.10 The Excited States of the Hydrogen Molecule

We shall now see what the molecular orbital theory can tell us about the excited electronic states of the hydrogen molecule. According to the simple LCAO treatment we have obtained two orbitals ψ_1 and ψ_2 [Eq. (7.72)]. In the ground state, both the electrons occupy the orbital ψ_1. The first excited state configuration above the ground state should result when an electron is promoted from the orbital ψ_1 to ψ_2. For the configuration $\psi_1^1\psi_2^1$, the following functions can be constructed.

$$\chi_1 = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)]$$

$$\chi_1' = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] \tag{7.127}$$

If $\hat{P}$ is an operator that interchanges the electronic coordinates, then

$$\hat{P}\chi_1 = \frac{1}{\sqrt{2}}[\psi_1(2)\psi_2(1) + \psi_1(1)\psi_2(1)] = \chi_1$$

$$\hat{P}\chi_1' = \frac{1}{\sqrt{2}}[\psi_1(2)\psi_2(1) - \psi_1(1)\psi_2(2)] = -\chi_1'$$

Thus, χ_1 and χ_1' are respectively symmetric and antisymmetric with respect to the interchange of electrons. For two electrons there are four possible spin-functions which can be multiplied with the above space functions to form the complete wavefunctions. The spin functions are:

$$\begin{aligned} \sigma_1 &= \alpha(1)\alpha(2) \\ \sigma_2 &= \beta(1)\beta(2) \\ \sigma_3 &= \alpha(1)\beta(2) \\ \sigma_4 &= \beta(1)\alpha(2) \end{aligned} \tag{7.128}$$

The eigenvalues of these functions for the operators $\hat{S}_z$, i.e.

$$\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$$

are respectively $+1$, -1, 0 and 0 in units of $h/2\pi$. The last two spin states in Eq. (7.128) clearly represent two equivalent spin states which are doubly degenerate. On operation with $\hat{P}$ we have

$$\hat{P}\sigma_3 = \hat{P}\alpha(1)\beta(2) = \alpha(2)\beta(1) = \sigma_4$$

$$\hat{P}\sigma_4 = \hat{P}\beta(1)\alpha(2) = \alpha(1)\beta(2) = \sigma_3$$

and hence

$$P(\sigma_3 + \sigma_4) = \sigma_3 + \sigma_4$$

$$P(\sigma_3 - \sigma_4) = -(\sigma_3 - \sigma_4)$$

It is, therefore, necessary to take the linear combination of the σ_3 and σ_4 functions. For a two-electron system the following four spin functions can be constructed.

$$\phi_S = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{7.129}$$

$$\phi_T = \begin{cases} \alpha(1)\alpha(2) \\ \dfrac{1}{\sqrt{2}}[\beta(1)\alpha(2) + \beta(2)\alpha(1)] \\ \beta(1)\beta(2) \end{cases} \tag{7.130}$$

where $1/\sqrt{2}$ is introduced for the normalisation of the spin functions. The function ϕ_S is called the spin function for the singlet state and has the eigenvalue -1 for the operator $\hat{P}$ and is, therefore, antisymmetric. The second set of functions ϕ_T have three components and is called the spin function for the triplet state. All these three components have the eigenvalue $+1$ of the operator $\hat{P}$ and are, therefore, symmetric. The total wavefunction including electron spin, according to the Pauli exclusion principle, must be antisymmetric. Thus we have the following combinations:

$$\begin{aligned} {}^1\Psi_1 &= \chi_1\phi_S \\ {}^3\Psi_1 &= \chi_1'\phi_T \end{aligned} \tag{7.131}$$

where the superscripts 1 and 3 denote the multiplicity of the states. Substituting for χ_1 and ϕ_S in Eq. (7.131), one obtains

$$\begin{aligned} {}^1\Psi_1 &= \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)]\,\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \frac{1}{2}[\psi_1(1)\alpha(1)\psi_2(2)\beta(2) - \psi_1(1)\beta(1)\psi_2(2)\alpha(2) \\ &\quad +\psi_1(2)\beta(2)\psi_2(1)\alpha(1) - \psi_1(2)\alpha(2)\psi_2(1)\beta(1)] \\ &= \frac{1}{2}[\{\psi_1(1)\bar{\psi}_2(2) - \psi_1(2)\bar{\psi}_2(1)\} - \{\bar{\psi}_1(1)\psi_2(2) - \bar{\psi}_1(2)\psi_2(1)\}] \\ &= \frac{1}{2}[\,|\,\psi_1(1)\bar{\psi}_2(2)\,| - |\,\bar{\psi}_1(1)\psi_2(2)\,|\,] \end{aligned} \tag{7.132}$$

Similarly, the wavefunctions of the triplet state may be written in the determinant form, as

$$\begin{aligned} &\frac{1}{\sqrt{2}}\,|\,\psi_1(1)\psi_2(2)\,| \\ {}^3\Psi_1 = &\frac{1}{\sqrt{2}}[|\,\psi_1(1)\bar{\psi}_2(2)\,| + |\,\bar{\psi}_1(1)\psi_2(2)\,|] \\ &\frac{1}{\sqrt{2}}\,|\,\bar{\psi}_1(1)\bar{\psi}_2(2)\,| \end{aligned} \tag{7.133}$$

We shall now evaluate the electronic energies of the excited states ${}^1\Psi_1$ and ${}^3\Psi_1$.

Since ${}^1\Psi_1$ is normalised,

$$E_{el}({}^1\Psi_1) = \langle {}^1\Psi_1 \mid H'_e \mid {}^1\Psi_1 \rangle \tag{7.134}$$

where H'_e is given by Eq. (7.69a).

It is to be remembered that this integral is over the entire spin-orbit space accessible to both the electrons. Substituting for ${}^1\Psi_1$,

$$E_{el}({}^1\Psi_1) = \iint 1/4[\mid \psi_1(1)\bar{\psi}_2(2) \mid - \mid \bar{\psi}_1(1)\psi_2(2) \mid] \mid H'_e \mid [\mid \psi_1(1)\bar{\psi}_2(2) \mid - \mid \bar{\psi}_1(1)\psi_2(2) \mid]\, d\tau_1\, d\tau_2 \tag{7.135}$$

We can separate this integral into two as follows

$$\begin{aligned} I_1 &= \iint [\mid \psi_1(1)\bar{\psi}_2(2) \mid \mid H'_e \mid \mid \psi_1(1)\bar{\psi}_2(2) \mid]\, d\tau_1\, d\tau_2 \\ &= \iint [\mid \bar{\psi}_1(1)\psi_2(2) \mid \mid H'_e \mid \mid \bar{\psi}_1(1)\psi_2(2) \mid]\, d\tau_1\, d\tau_2 \end{aligned} \tag{7.136}$$

and

$$\begin{aligned} I_2 &= \iint [\mid \psi_1(1)\bar{\psi}_2(2) \mid \mid H'_e \mid \mid \bar{\psi}_1(1)\psi_2(2) \mid]\, d\tau_1\, d\tau_2 \\ &= \iint [\mid \bar{\psi}_1(1)\psi_2(2) \mid \mid H'_e \mid \mid \psi_1(1)\bar{\psi}_2(2) \mid]\, d\tau_1\, d\tau_2 \end{aligned} \tag{7.137}$$

Therefore

$$E_{el}({}^1\bar{\psi}_1) = 1/4[2I_1 - 2I_2] = 1/2[I_1 - I_2] \tag{7.138}$$

Let us evaluate now the integrals I_1 and I_2. Expanding the determinants in I_1 we get

$$I_1 = \iint [\psi_1(1)\bar{\psi}_2(2) - \psi_1(2)\bar{\psi}_2(1)] \mid H'_e \mid [\psi_1(1)\bar{\psi}_2(2) - \psi_1(2)\, \bar{\psi}_2(1)]\, d\tau_1\, d\tau_2 \tag{7.139}$$

Putting $\psi_1(1)\bar{\psi}_2(2) = A$, $\psi_1(2)\bar{\psi}_2(1) = B$, Eq. (7.139) can now be written in the bracket notation as

$I_1 = \langle A \mid H'_e \mid A \rangle + \langle B \mid H'_e \mid B \rangle - \langle A \mid H'_e \mid B \rangle - \langle B \mid H'_e \mid A \rangle$

Since H' is hermitian, i.e. $\langle A \mid H'_e \mid B \rangle = \langle B \mid H'_e \mid A \rangle$, we write I_1 as

$$I_1 = \langle A \mid H'_e \mid A \rangle + \langle B \mid H'_e \mid B \rangle - 2\langle A \mid H'_e \mid B \rangle \tag{7.140}$$

We will now examine the typical integrals in more details. Substituting for H'_e, Eq. (7.69a), the integral $\langle A \mid H'_e \mid A \rangle$ may be written as follows

$$\begin{aligned} \langle A \mid H'_e \mid A \rangle &= \langle \psi_1(1)\bar{\psi}_2(2) \left| \left(H^c(1) + H^c(2) + \frac{1}{r_{12}} \right) \right| \psi_1(1)\bar{\psi}_2(2) \rangle \\ &= \langle \psi_1(1) \mid H^c(1) \mid \psi_1(1) \rangle \langle \bar{\psi}_2(2) \mid \bar{\psi}_2(2) \rangle \\ &\quad + \langle \bar{\psi}_2(2) \mid H^c(2) \mid \bar{\psi}_2(2) \rangle \langle \psi_1(1) \mid \psi_1(1) \rangle \\ &\quad + \langle \psi_1(1)\bar{\psi}_2(2) \left| \frac{1}{r_{12}} \right| \psi_1(1)\bar{\psi}_2(2) \rangle \end{aligned} \tag{7.141}$$

Since the spin functions as well as the orbital functions are normalised, using the same symbolism as before we have

$$\langle A \mid H'_e \mid A \rangle = E_1 + E_2 + J_{12} \tag{7.142}$$

where J_{12} describes the repulsion between the electron 1 in orbital ψ_1 and the electron 2 in orbital ψ_2. The same procedure gives

$$\langle B \mid H'_e \mid B \rangle = E_1 + E_2 + J_{12} \tag{7.143}$$

However, the integral

$$\begin{aligned} \langle B \mid H'_e \mid A \rangle = \langle A \mid H'_e \mid B \rangle &= \langle \psi_1(1) \mid H^c(1) \mid \bar{\psi}_2(1) \rangle \langle \bar{\psi}_2(2) \mid \psi_1(2) \rangle \\ &+ \langle \bar{\psi}_2(2) \mid H^c(2) \mid \psi_1(2) \rangle \langle \psi_1(1) \mid \bar{\psi}_2(1) \rangle \\ &+ \langle \psi_1(1)\bar{\psi}_2(2) \left| \frac{1}{r_{12}} \right| \psi_1(2)\bar{\psi}_2(1) \rangle = 0 \end{aligned} \tag{7.144}$$

because of the orthogonality of the spin and orbital functions, thus,

$$I_1 = 2E_1 + 2E_2 + 2J_{12} \tag{7.145}$$

Expanding the determinants in I_2, [see Eq. (7.137)] one gets

$$\begin{aligned} I_2 &= \iint [\psi_1(1)\bar{\psi}_2(2) - \psi_1(2)\bar{\psi}_2(1)] H'_e [\bar{\psi}_1(1)\psi_2(2) - \bar{\psi}_1(2)\psi_2(1)] \, d\tau_1 \, d\tau_2 \\ &= \langle A \mid H'_e \mid C \rangle - \langle A \mid H'_e \mid D \rangle - \langle B \mid H'_e \mid C \rangle + \langle B \mid H'_e \mid D \rangle \end{aligned} \tag{7.146}$$

where A and B are already defined and C and D are given by

$$\bar{\psi}_1(1)\psi_2(2) = C \quad \text{and} \quad \bar{\psi}_1(2)\psi_2(1) = D$$

It may be easily seen that the first and the fourth integrals in Eq. (7.146) vanish owing to the orthogonality of the spin functions, while the second and third integrals are equal and can be written as

$$\begin{aligned} \langle A \mid H'_e \mid D \rangle &= \langle B \mid H'_e \mid C \rangle \\ &= \langle \psi_1(1)\bar{\psi}_2(2) \left| \frac{1}{r_{12}} \right| \bar{\psi}_1(2)\psi_2(1) \rangle \end{aligned} \tag{7.147}$$

This again involves repulsion between two electrons, but the electron 1 is associated with both the orbitals ψ_1 and ψ_2 and so is electron 2. It is as though electrons were exchanged between two orbitals and, therefore, the integrals of this type usually denoted by the symbol K, are called exchange integral. Thus, we have

$$I_2 = -2K_{12} \tag{7.148}$$

It is to be noted that if any one electron is associated with two orbitals that involve different spin functions then the exchange integral vanishes. The energy, E_{el} of the singlet excited state, ${}^1\Psi_1$ of the hydrogen molecule is obtained after substituting for I_1 and I_2 from Eqs. (7.145) and (7.148) in Eq. (7.138). Then one obtains

$$E_{el}({}^1\Psi_1) = E_1 + E_2 + J_{12} + K_{12} \tag{7.149}$$

Starting with any one component of the triplet state wavefunctions [Eq. (7.133)] and, following the similar procedure, one obtains

$$E_{el}(^3\Psi_1) = E_1 + E_2 + J_{12} - K_{12} \tag{7.150}$$

The energy difference between the singlet and triplet states is $2K_{12}$ and since both J and K integrals represent the electron repulsion terms, the triplet state is more stable. This demonstrates that the states of highest spin multiplicity have the maximum stability (Hund's rule).

7.11 The Electronic Transition in the Hydrogen Molecule

When electromagnetic radiation is absorbed by a molecule it promotes the molecule from its ground state to an excited state. The energy required to effect this transition is, of course, the energy absorbed. Thus, we expect the molecule to absorb radiation of particular wavelength corresponding to the energy difference between the ground and the excited states. However, the probability of such a transition depends on the square of the transition dipole moment integral defined as (in a.u.).

$$\langle \Psi_g \mid \sum_i r_i \mid \Psi_{ex} \rangle$$

where r_i is the position vector of the electron i in a molecule, Ψ_g and Ψ_{ex} are respectively the ground and the excited state wavefunctions of the molecule concerned. In this definition the summation in the integral is over all the electrons present in the molecule.

Let us consider the transition from the singlet ground state Ψ_0 to the excited triplet state $^3\Psi_1$ of the hydrogen molecule. The transition dipole moment is given by

$$M(\Psi_0 \rightarrow {}^3\Psi_1) = \langle \Psi_0 \mid \sum_i r_i \mid {}^3\Psi_1 \rangle$$

This integral is over the spin-orbit space. On separating the spin-functions and the orbital functions, one may write, using Eqs. (7.87), (7.129) and (7.131).

$$\Psi_0 = \chi_0 \phi_S$$

$$^3\Psi_1 = \chi_1' \phi_T$$

where $\chi_0 = \psi_1(1)\psi_1(2)$ and χ_1' is defined by Eq. (7.127)
Hence

$$M(\Psi_0 \rightarrow {}^3\Psi_1) = \langle \chi_0 \mid \Sigma r_i \mid \chi_1' \rangle \langle \phi_S \mid \phi_T \rangle \tag{7.151}$$

where the two integrals refer separately to the orbital and spin coordinates of electron. Since the spin functions ϕ_S and ϕ_T are orthogonal, the second integral in Eq. (7.151) is zero. Transition from a singlet to a triplet state is, therefore, always forbidden. If, however, the spin and the orbital functions cannot be separated owing to the spin-orbit interaction, the transition dipole moment M may not be zero.

We shall now compute the transition dipole moment of an optical transition in the hydrogen molecule from the ground singlet, Ψ_0 to an excited singlet ${}^1\Psi_1$. On separating the spin and the orbital functions as before, one may write

$$M(\Psi_0 \rightarrow {}^1\Psi_1) = \langle \chi_0 \mid \sum_i r_i \mid \chi_1 \rangle \langle \phi_S \mid \phi_S \rangle \tag{7.152}$$

Since the spin function ϕ_S is normalised, the second integral in Eq. (7.152) is unity. So we need to evaluate the first integral. Inserting for χ_0 and χ_1 their appropriate expressions, one gets

$$\begin{aligned} M(\Psi_0 \rightarrow {}^1\Psi_1) &= \frac{1}{\sqrt{2}} \langle \psi_1(1)\psi_1(2) \mid (\vec{r}_1 + \vec{r}_2) \mid [\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)] \rangle \\ &= \frac{1}{\sqrt{2}} [\langle \psi_1(1)\psi_1(2) \mid \vec{r}_1 \mid \{\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\} \rangle \\ &\quad + \langle \psi_1(1)\psi_1(2) \mid \vec{r}_2 \mid \{\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)\} \rangle] \\ &= \frac{1}{\sqrt{2}} [\langle \psi_1(1) \mid \vec{r}_1 \mid \psi_1(1) \rangle \langle \psi_1(2) \mid \psi_2(2) \rangle \\ &\quad + \langle \psi_1(1) \mid \vec{r}_1 \mid \psi_2(1) \rangle \langle \psi_1(2) \mid \psi_1(2) \rangle \\ &\quad + \langle \psi_1(2) \mid \vec{r}_2 \mid \psi_2(2) \rangle \langle \psi_1(1) \mid \psi_1(1) \rangle \\ &\quad + \langle \psi_1(2) \mid \vec{r}_2 \mid \psi_1(2) \rangle \langle \psi_1(1) \mid \psi_2(1) \rangle \end{aligned} \tag{7.153}$$

Due to the orthogonality of the orbitals ψ_1 and ψ_2 the second and third terms in Eq. (7.153) remain non-vanishing. Thus

$$M(\Psi_0 \rightarrow {}^1\Psi_1) = \frac{1}{\sqrt{2}} [\langle \psi_1(1) \mid \vec{r}_1 \mid \psi_2(1) \rangle + \langle \psi_1(2) \mid \vec{r}_2 \mid \psi_2(2) \rangle] \tag{7.154}$$

Since there is nothing to distinguish between the electron 1 and the electron 2, the two integrals in Eq. (7.154) are equivalent.

$$M(\Psi_0 \rightarrow {}^1\Psi_1) = \sqrt{2} \cdot \langle \psi_1(1) \mid \vec{r}_1 \mid \psi_2(1) \rangle \tag{7.155}$$

Substituting for ψ_1 and ψ_2 from Eqs. (7.46), (7.47)

$$\begin{aligned} M(\Psi_0 \rightarrow {}^1\Psi_1) &= \sqrt{2} \, \frac{1}{\sqrt{2(1+S)}} \cdot \frac{1}{\sqrt{2(1-S)}} \\ &\quad \times \langle \{1s_a(1) + 1s_b(1)\} \mid \vec{r}_1 \mid \{1s_a(1) - 1s_b(1)\} \rangle \\ &= \frac{\sqrt{2}}{\sqrt{4(1-S^2)}} [\langle 1s_a(1) \mid \vec{r}_1 \mid 1s_a(1) \rangle \\ &\quad - \langle 1s_b(1) \mid \vec{r}_1 \mid 1s_b(1) \rangle] \end{aligned} \tag{7.156}$$

The first integral in Eq. (7.156) determines the mean position of an electron in 1*s* atomic orbital which is centred on atom *a*. Since the orbital is spherically symmetrical, the position of an electron coincides the position of the nucleus *a*. Similarly, according to the second integral in Eq. (7.156) the mean position of an electron in $1s_b$ is the position of the nucleus, *b*. Thus

$$M(\Psi_0 \rightarrow {}^1\Psi_1) = \frac{\sqrt{2}}{\sqrt{4(1 - S^2)}}[\vec{r_a} - \vec{r_b}] \tag{7.157}$$

where $\vec{r_a}$ and $\vec{r_b}$ are the position vectors of nuclei *a* and *b* respectively. Therefore

$$M(\Psi_0 \rightarrow {}^1\Psi_1) = \frac{|R|}{\sqrt{2(1 - S^2)}} \tag{7.158}$$

where *R* is the bond length in the hydrogen molecule.

7.12 Molecular Orbitals of the Homonuclear Diatomic Molecules

A qualitative but satisfactory molecular orbital treatment of homonuclear diatomic molecules is mainly due to Lennard-Jones[18]. We have seen that when we bring two similar atom together each atomic level ϕ_a (or ϕ_b) splits into two whose LCAO forms are $\phi_a + \phi_b$ and $\phi_a - \phi_b$. One of these is usually bonding and the other antibonding. For the *s*-type orbitals the boundary contours for the bonding and antibonding orbitals are shown in Fig. 7.12.

When two sets of 2*p*-atomic orbitals overlap, six molecular orbitals are obtained. We can have the 2*p*-atomic orbitals pointing towards each other along the internuclear axis (let us call it the *z*-axis). The boundary contours of the bonding orbital $2p_{za} + 2p_{zb}$ and the antibonding orbital $2p_{za} - 2p_{zb}$ are also shown in Fig. (7.12). If we combine together two $2p_y$-orbitals we get two molecular orbitals as before but they have nodes passing through the molecular axis (i.e., *z*-axis). The combination of two $2p_x$-orbitals leads precisely to the similar molecular orbitals as before except that they are turned through 90° around the molecular axis. Since the *x* and *y*-axes are equivalent in space the corresponding molecular orbitals $(2p_{ya} + 2p_{yb})$ and $(2p_{ya} - 2p_{yb})$ must be, by symmetry, degenerate with their *x*-counterparts.

The molecular orbitals of a homonuclear diatomic molecule are usually described in terms of a few symmetry symbols in a way similar to that in which atomic orbitals are described by a few quantum numbers. It has been shown that atomic hamiltonian (spin free) commutes with $\hat{L}^2$ and $\hat{L}_z$ and therefore it is possible to specify not only the total angular momentum but also a component of total angular momentum of an electron in a given energy state of an atom. Thus atomic orbitals are labelled by two angular

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[18] J.E. Lennard-Jones, *Trans. Faraday Soc.*, **25**, 668, 1929.

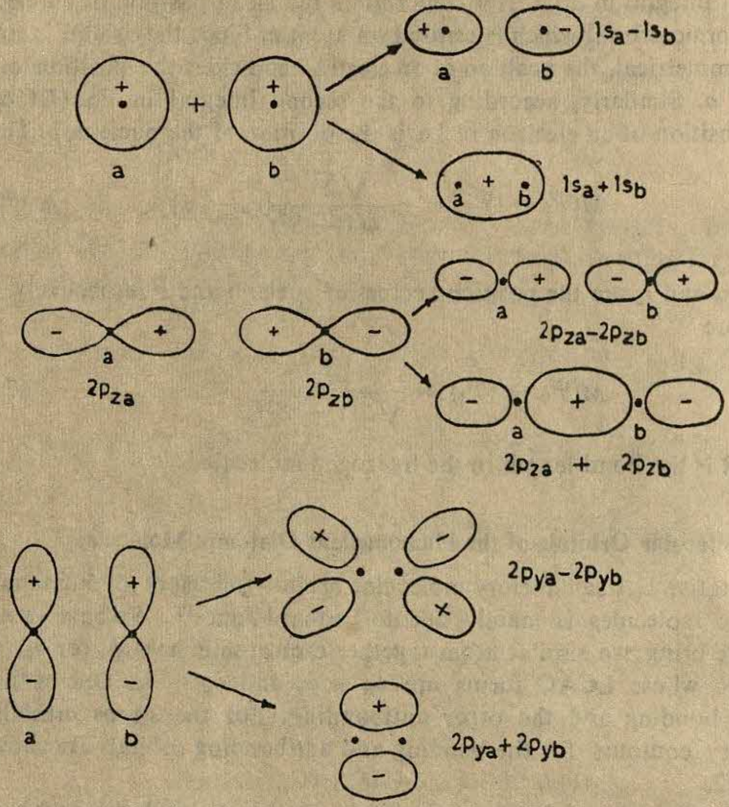

Fig. 7.12 *The boundary contours of the bonding and antibonding molecular orbitals in homonuclear diatomics.*

momentum symbols l and m. For each l there are $2l + 1$ values of m, all having same energy.

When an atom is placed in an external electric field of uniform field strength ϵ_z (assuming the direction of the field in the z-direction), the $(2l + 1)$ fold degeneracy of atomic orbitals is lost through the interaction between the field and the induced atomic dipole. An atom does not possess any permanent dipole moment but the induced dipole μ_z is related to ϵ_z through the polarizability α of the atom as

$$\mu_z = \alpha\epsilon_z \tag{7.159}$$

The interaction energy of the electric field with this dipole is given by

$$\Delta E = -\mu_z\epsilon_z = -\alpha\cdot\epsilon_z^2 \tag{7.160}$$

This means that reversing the field direction does not change the energy. In other words, atomic levels with ± m have the same energy in the presence of an electric field. So, the orbitals with different values of $|m|$ will have different energies in the presence of an external electric field. This phenomenon is known as the Stark effect. From the condition under which the molecular hamiltonian commutes with $\hat{L}_z$, it is possible to say, as an analogy, that the symmetry of a diatomic or a linear polyatomic molecule is the same as that of an atom in the presence of an axial electric field.

We shall now examine the condition under which the molecular hamiltonian commutes with $\hat{L}_z$. For this, one needs to show when the potential energy term, i.e., V commutes with $\hat{L}_z$. This molecular potential energy may be written as (in a.u.)

$$V = \sum_{i}^{\text{electrons}} \sum_{a}^{\text{nuclei}} \frac{1}{r_{ia}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \tag{7.161}$$

where r_{ia} is the distance between a^{th} nucleus and i^{th} electron and r_{ij}, the interelectronic distance. In cylindrical polar coordinates $\hat{L}_z$ is given by

$$\hat{L}_z = \frac{h}{2\pi i}\left(\frac{\partial}{\partial \varphi_1} + \frac{\partial}{\partial \varphi_2} + \frac{\partial}{\partial \varphi_3} + \ldots\right) \tag{7.162}$$

In atoms, the operator $\hat{L}_z$ commutes with the $1/r_{ij}$ terms in the hamiltonian (see Sec. 6.10). Since r_{ij} depends on the electronic coordinates only, $\hat{L}_z$ should commute with the $1/r_{ij}$ terms in the molecular hamiltonian also.

Let us consider, for simplicity, only one electron in a molecule, then

$$\hat{L}_z = \frac{h}{2\pi i} \frac{\partial}{\partial \varphi i}$$

Suppose, ψ be the molecular wavefunction, then consider

$$\hat{L}_z\left(\frac{1}{r_{ia}}\psi\right) = \frac{h}{2\pi i} \frac{\partial}{\partial \varphi i} \left(\frac{1}{r_{ia}}\psi\right)$$

$$= \frac{h}{2\pi i} \frac{1}{r_{ia}} \cdot \frac{\partial \psi}{\partial \varphi_i} + \frac{h}{2\pi i} \psi \frac{\partial}{\partial \varphi_i}\left(\frac{1}{r_{ia}}\right)$$

$$\hat{L}_z \frac{1}{r_{ia}} = \frac{1}{r_{ia}} \hat{L}_z + \frac{h}{2\pi i} \frac{\partial}{\partial \varphi i}\left(\frac{1}{r_{ia}}\right) \tag{7.163}$$

This shows that $\hat{L}_z$ can commute with the hamiltonian if r_{ia} is independent of φ_i. If we consider an atom 'a' on the z-axis (Fig. 7.13) then r_{ia} is independent of φ_i. If other nuclei in a molecule also lie on the same z-axis then r_{ib}, etc., will also be independent of φ_i. Therefore, $\hat{L}_z$ (i.e. angular momentum component along the molecular axis) can commute with the molecular hamiltonian if the molecule is linear.

The H_2^+ is the simplest example of a linear molecule for which the very accurate solution of the Schrödinger equation is obtained by elaborate calculations. The wave equation in a.u. is

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}\right)\psi = E\psi$$

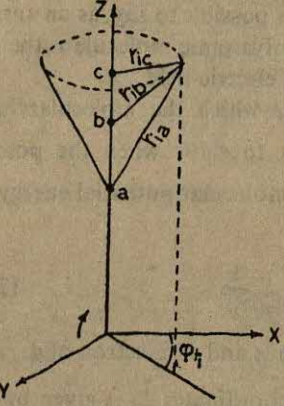

Fig. 7.13 *Cylindrical coordinates of electron and nuclei in a linear molecule.*

where R is the internuclear distance. Introducing the following coordinates

$$\xi = \frac{r_a + r_b}{R}, \quad 1 \leqslant \xi \leqslant \infty$$

$$\eta = \frac{r_a - r_b}{R}, \ -1 \leqslant \eta \leqslant 1$$

and φ, an azimuthal angle about the molecular axis (Fig. 7.13) $0 \leqslant \varphi \leqslant 2\pi$, then the wavefunction can be separated into three equations each of which contains only one of the three variables ξ, η, φ. These equations have been solved by Teller, Burrau and later by Bates[19] and others for the ground state and several low lying excited states leading to results in good agreement with experiment. The method of solution will not be described here. The equation in φ has been shown to be of the form

$$\frac{\partial^2 \Phi}{\partial \varphi^2} = -\lambda^2 \Phi(\varphi) \tag{7.164}$$

The normalised solutions of this equation are:

$$\Phi = \frac{1}{\sqrt{2\pi}} \exp(i\lambda\varphi) \tag{7.165}$$

where λ can take on positive or negative integral values. The energy is shown to depend on λ through λ^2 so that except when $\lambda = 0$, the orbitals are all doubly degenerate corresponding to $\pm\lambda$. Orbitals of a diatomic molecule can, therefore, be described in the form

$$\psi = F(\xi, \eta) \exp(\pm i\lambda\varphi) \tag{7.166}$$

and these functions can be shown to be the eigenfunctions of $\hat{L}_z$ as

$$\hat{L}_z \psi = \frac{h}{2\pi i} \frac{\partial \psi}{\partial \varphi} = \frac{h}{2\pi i} F(\xi, \eta) \exp(\pm i\lambda\varphi)(\pm i\lambda) = \pm \lambda \frac{h}{2\pi} \psi \tag{7.167}$$

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[19] D.R. Bates et al., *Phil. Trans. R. Soc., London*, **246A**, 215, 1953.

Except when $\lambda = 0$, all the doubly degenerate orbitals have positive and negative components of angular momentum along the internuclear axis. This situation is analogous to the behaviour of atomic states in an axial electric field where the atomic states with $\pm m$ are degenerate. Therefore, a diatomic molecule can be compared with an atom in an electric field and the quantum number λ is analogous to m and not l.

When $R = 0$, the wave equation of H_2^+ becomes that of He^+ and the quantum number λ becomes equivalent to the atomic quantum number m. Therefore, the quantum number λ is a good quantum number for the description of molecular orbitals at all internuclear distances. A molecular orbital is characterised by its value of λ in the following way

$$\lambda = 0, 1, 2, 3, \ldots$$
$$\text{Orbital type} = \sigma, \pi, \delta, \rho$$

These angular momentum symbols apply equally to both homo and heteronuclear diatomic molecules. Since for the united atom the possible values of m are 0, 1, 2, 3, 4, . . . and if the molecular orbital is to be designated by the states of the united atom to which it reduces, then the possible molecular orbitals are $1s_\sigma$, $2s\sigma$, $2p_\sigma$, $2p_\pi$, $3s_\sigma$, $3p_\sigma$, $3p_\pi$, etc. In Fig. 7.14 are plotted the adiabatic potential curves of H_2^+ for the orbitals $1s_\sigma$ and $2p_\sigma$, the two lowest states. It is seen that the $1s_\sigma$ state corresponds to the LCAO from $(1s_a + 1s_b)$ and the $2p_\sigma$ state to $(1s_a - 1s_b)$ of our earlier treatment.

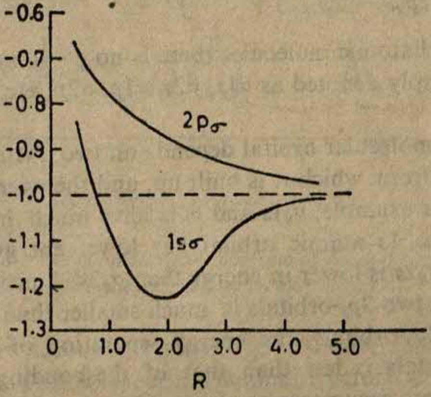

Fig. 7.14 *Adiabatic potential energy curves of H_2^+. Energies and R are expressed in a.u.*

For molecules other than H_2^+ the wavefunction of the form of Eq. (7.166) cannot be used. The convenient form for such molecules is the LCAO form of molecular orbitals. Moreover, according to the very commonly used scheme, the molecular orbitals are labelled by the atomic orbitals into which they dissociate when the nuclei are pulled apart. Since homonuclear diatomic molecules have higher symmetry ($D_{\infty h}$) than heteronuclear ($C_{\infty v}$), their orbitals may be further classified by their behaviour on inversion through the centre of symmetry. Thus, for a homonuclear diatomic molecule, the orbital of the form $1s_a + 1s_b$ is symmetric, and $1s_a + 1s_b$ is antisymmetric with respect to the inversion through the centre of symmetry. These two orbitals are said to have *g* and *u*-symmetry respectively. Therefore, these two orbitals are represented symbolically as

$$1s_a + 1s_b \approx \sigma_g\, 1s$$

$$1s_a - 1s_b \approx \sigma_u\, 1s$$

These are σ-orbitals because $m = 0$ for $1s$-electron in an atom, and since the molecular orbitals we are dealing with are one-electron orbitals, $\lambda = 0$. Similarly, one obtains

$$\left.\begin{aligned} 2s_a + 2s_b &\approx \sigma_g\, 2s \\ 2s_a - 2s_b &\approx \sigma_u\, 2s \\ 2p_{za} + 2p_{zb} &\approx \sigma_g\, 2p \\ 2p_{za} - 2p_{zb} &\approx \sigma_u\, 2p \end{aligned}\right\} \lambda = 0$$

$$\left.\begin{array}{l} \left.\begin{array}{l} 2p_{xa} + 2p_{xb} \\ 2p_{ya} + 2p_{yb} \end{array}\right\} \pi_u 2p \\ \left.\begin{array}{l} 2p_{xa} - 2p_{xb} \\ 2p_{ya} - 2p_{yb} \end{array}\right\} \pi_g 2p \end{array}\right\} \lambda = \pm 1 .$$

For heteronuclear diatomic molecules there is no $g - u$ symmetry and these orbitals will be simply denoted as $\sigma 1s$, $\sigma 2s$, $\sigma 1p$, $\sigma 2p$, etc. or sometimes 1σ, 2σ, 3σ, etc.

The energy of a molecular orbital depends on two factors, viz. the type of atomic orbital from which it is built up, and the overlap between these atomic orbitals. For example, $\sigma_g 1s$ and $\sigma_u 1s$ have much lower energy than $\sigma_g 2s$ simply because $1s$ atomic orbital has lower energy than $2s$ atomic orbital. Similarly, $\sigma_g 2s$ is lower in energy than $\sigma_g 2p$. Since the overlap between two $2p_x$- or two $2p_y$-orbitals is much smaller than that between two $2s$-orbitals or two $2p_z$-orbitals, the energy separation of the bonding and antibonding π orbitals is less than that of the bonding and antibonding σ-orbitals. From these arguments one may arrive at the following order of the molecular orbital energies.

$$\sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s < \sigma_g 2p < \sigma_u 2p < \sigma_g 2p < \sigma_u 2p \qquad (7.168)$$

This order is, however, subject to change depending on the extent of interaction between $2s - 2p_z$ atomic orbitals. Once the order of energy levels is known, the same principle which is used to build up the electronic configuration of atoms may now be used for the homonuclear diatomic molecules and its ions.

The energy ordering of the MOs was first inferred by Mulliken[20] in 1932 from a study of molecular electronic spectra. The more striking evidence for the energy ordering comes from photoelectron spectroscopy. This is conceptually based on photoelectric effect discussed in Chap. 1. Suppose a radiation of frequency ν, and therefore of energy $h\nu$, hits a molecule and releases an electron with binding energy ϵ. If we neglect the small recoil then from the conservation of energy, the kinetic energy T of the ejected electron is given by

$$T = h\nu - \epsilon$$

By selecting ν of the incident radiation and then measuring T one can determine ϵ, which by Koopman's theorem is the ionisation energy of the MO. The energy $h\nu$ must be greater than ϵ. One uses the vacuum ultraviolet radiation to release the valence electrons. Figure 7.15 shows the photoelectron spectra of N_2 and reveals four distinct valence-electron ionisation potentials corresponding to removal of an electron from $\sigma_g 2s$, $\sigma_u 2s$, $\pi_u 2p$ and $\sigma_g 2p$. From a careful study of the four peaks it is possible to identify the symmetry of the relevant MOs and also to determine the sequence of energies. It is found that in N_2 the $\sigma_g 2p$ MO has higher energy (or lower ionisation potential) than $\pi_u 2p$ while in O_2 the ordering is reversed.

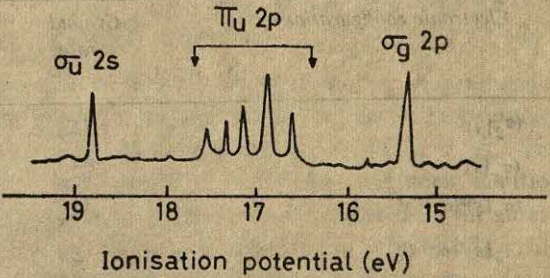

Fig. 7.15 *The photoelectron spectrum of N_2 showing the three distinct occupied valence shell molecular orbitals.*

A comprehensive account of molecular photoelectron spectroscopy has been prepared by Turner et al[21]. The fine structure which is observed for the $\pi_u 2p$ MO arises from the vibrational energy levels of the ionised species and is useful for the assignment.

For diatomics having many electrons, the electronic state is described by the total spin angular momentum and total orbital angular momentum along the internuclear axis. The total spin multiplicity $2S + 1$ is written as superior prefix as for atomic states. The total orbital angular momentum is indicated by capital Greek letters according to the following scheme

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[20] R.S. Mulliken, *Rev. Mod. Phys.*, 4, 1, 1932.

[21] D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley, New York, 1970.

$$\sum_i \lambda_i = 0, 1, 2, 3, \ldots$$

$$\Sigma, \pi, \Delta, \Phi, \ldots$$

An electron configuration in which all orbitals are doubly filled is called a closed shell configuration which will always have ${}^1\Sigma_g$ symbol because there must be as many electrons with α spin as with β spin and as many with angular momentum of $+\lambda h/2\pi$ as with $-\lambda h/2\pi$. Besides, the overall symmetry of a state to inversion is obtained by multiplying all the symmetries of the individual electrons according to the scheme

$$g \times g = g \qquad u \times u = g \qquad g \times u = u$$

Table 7.2 shows the ground state electron configuration of some homonuclear diatomic molecules and some positive ions. The bond energy depends approximately on the net excess of electrons in bonding orbitals over those in antibonding orbitals. Thus, the dissociation energy of H_2 is about twice that of H_2^+. In He_2 and Be_2 the number of bonding and antibonding electrons is the same. Therefore, they are not stable in their ground state although some excited states may exist with a positive dissociation energy relative to one excited and one ground state atom. The N_2 molecule has the largest bond dissociation energy in the series of molecules shown in Table 7.2

TABLE 7.2 THE GROUND STATES OF SOME HOMONUCLEAR DIATOMICS

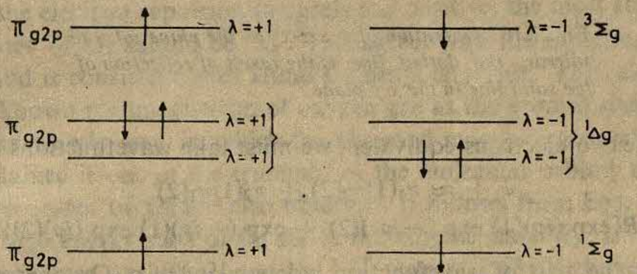
Molecule	*Electronic configuration**	*Ground state*	*Dissociation** energy (eV)*
H_2^+	$(\sigma_g 1s)^1$	${}^2\Sigma_g$	2.65
H_2	$(\sigma_g 1s)^2$	${}^1\Sigma_g$	4.48
He_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	${}^1\Sigma_g$	—
He_2^+	$(\sigma_g 1s)^2(\sigma_u 1s)^1$	${}^2\Sigma_u$	3.10
Li_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2$	${}^1\Sigma_g$	1.14
Be_2	$[Li_2](\sigma_u 2s)^2$	${}^1\Sigma_g$	—
B_2	$[Li_2](\sigma_u 2s)^2(\pi_u 2p)^2$	${}^3\Sigma_g$	3.0 ± 0.6
C_2	$[Li_2](\sigma_u 2s)^2(\pi_u 2p)^4$	${}^1\Sigma_g$	4.9 ± 0.3
N_2	$[Be_2](\pi_u 2p)^4(\sigma_g 2p)^2$	${}^1\Sigma_g$	9.6
N_2^+	$[Be_2](\pi_u 2p)^4(\sigma_g 2p)^1$	${}^2\Sigma_g$	8.73
O_2	$[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$	${}^3\Sigma_g$	5.88
O_2^+	$[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^1$	${}^2\pi_g$	6.48
F_2	$[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4$	${}^1\Sigma_g$	1.6 ± 0.4
F_2^+	$[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^3$	${}^2\pi_g$	—

*Because of $2s - 2p$ interaction it is found that for the lighter molecules except for O_2 and F_2 the positions of orbitals $\sigma_g 2p$ and $\pi_u 2p$ are interchanged in the series of Eq. (7.168).

**A.G. Gaydon, *Dissociation Energies*, Chapman and Hall, 1953.

because it has the largest excess (six) of bonding electrons over antibonding electrons. When an electron is removed to form N_2^+ the bond becomes weaker. On the other hand, in O_2, the highest partly filled orbital $\pi_g 2p$ is an antibonding orbital with two electrons. If one of these is removed, the system (i.e., O_2^+) has the larger net excess of bonding electrons than O_2. For this reason the bond in O_2^+ is stronger and shorter than that in O_2.

We shall now deal with O_2 in more detail because its electron configurations can give rise to more than one electronic state depending on how the spin and orbital angular momenta of the outer two electrons are arranged. In O_2, except for the orbital $\pi_g 2p$, all other orbitals are completely filled. The net contribution of these orbitals to the spin or orbital angular momentum is zero. Since $\pi_g 2p$ is doubly degenerate, two electrons can be allocated in these orbitals, taking into account the Pauli exclusion principle, in the following three ways.



Here, the arrows ↑ and ↓ denote electrons with spin quantum number $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively. The configuration π_g^2 for a homonuclear diatomic molecule therefore gives rise to three states $^3\Sigma_g$, $^1\Delta_g$ and $^1\Sigma_g$. There is, however, one more symmetry operation which has not been mentioned so far. This is a reflection from a plane ($\varphi = 0$) containing the internuclear axis and is denoted by σ_v. Since all the σ-orbitals are symmetric to this operation, this operation is redundant. However, when we have two electrons occupying the degenerate pair of π orbitals such that their orbital angular momenta cancel, this symmetry operation becomes informative. Suppose, π_1 and π_2 are the components of the degenerate π orbital. Since these orbitals are made up of two different types of $2p$-atomic orbitals for which $m = \pm 1$, the molecular orbitals π_1 and π_2 have the factor $\exp(i\varphi)$ and $\exp(-i\varphi)$ where φ is the azimuthal angle about the molecular axis (Fig. 7.13). The operation σ_v changes φ to $(2\pi - \varphi)$ (see Fig. 7.16 where $z - x$ is the plane of the mirror). Then

$$\sigma_v \exp(\pm i\varphi) = \exp[\pm i(2\pi - \varphi)] = \exp(\pm i\varphi) \tag{7.169}$$

since

$$\exp(2\pi i) = 1 \tag{7.170}$$

There are two electronic arrangements of the type

$$\pi_1(1)\pi_2(2)$$
$$\pi_1(2)\pi_2(1)$$

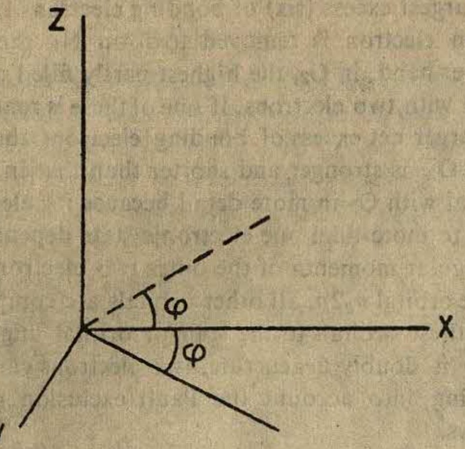


Fig. 7.16 *Operation of* σ_v. *z-x is the plane of the mirror, the dotted line is the result of reflection of the solid line in the x-y plane*

To make the two electrons equivalent we must take wavefunctions as

$$\psi \pm \approx \pi_1(1)\pi_2(2) \pm \pi_2(1)\pi_1(2)$$
$$\approx R\{\exp(i\varphi)(1)\exp(-i\varphi)(2) \pm \exp(-i\varphi)(1)\exp(i\varphi)(2)\}$$

where R is the part of wavefunction independent of φ. On operation with σ_v one obtains

$$\left.\begin{aligned}\sigma_v\psi_+ &= R\{\exp(-i\varphi)(1)\exp(i\varphi)(2) + \exp(i\varphi)(1)\\ &\quad \exp(-i\varphi)(2)\} = \psi_+\\ \sigma_v\psi_- &= R\{\exp(-i\varphi)(1)\exp(i\varphi)(2) - \exp(i\varphi)(1)\\ &\quad \exp(-i\varphi)(2)\} = -\psi_-\end{aligned}\right\} \quad (7.171)$$

Both ψ_+ and ψ_- stand for Σ_g state in O_2. Since, according to the Pauli exclusion principle, total wavefunction including spin must be antisymmetric, ψ_+ (hence Σ_g^+) must be associated with antisymmetric spin function and ψ_- (hence Σ_g^-) with symmetric spin functions. Therefore, three electronic states of O_2 are symbolised as $^3\Sigma_g^-$, $^1\Sigma_g^+$, $^1\Delta_g$.

In the evaluation of the energies of these three states of O_2 we shall consider only the open shell configuration, e.g. $(\pi_g 2p)^2$, and leave other orbitals that are completely filled out of account because the latter orbitals make roughly the same contributions to the energies of three states. Therefore, the procedure of evaluating the relative energies of the electronic states of O_2 is the same as described earlier in this chapter for the ground and excited states of H_2. Thus one obtains

$$\left.\begin{aligned}E_{el}(^1\Delta_g) &= 2\epsilon + J\pi_1\pi_1 = 2\epsilon + J\pi_2\pi_2\\ E_{el}(^1\Sigma_g^+) &= 2\epsilon + J\pi_1\pi_2 + K\pi_1\pi_2\\ E_e(^2\Sigma_g^-) &= 2\epsilon + J\pi_1\pi_2 - K\pi_1\pi_2\end{aligned}\right\} \quad (7.172)$$

where ϵ is the energy of the component orbitals π_1(or π_2) of $\pi_g 2p$, J and K are the coulomb and exchange integrals defined as

$$J\pi_1\pi_1 = \left\langle \pi_1(1)\pi_1(2) \left| \frac{1}{r_{12}} \right| \pi_1(1)\pi_1(2) \right\rangle$$

$$J\pi_2\pi_2 = \left\langle \pi_2(1)\pi_2(2) \left| \frac{1}{r_{12}} \right| \pi_2(1)\pi_2(2) \right\rangle$$

$$J\pi_1\pi_2 = \left\langle \pi_1(1)\pi_2(2) \left| \frac{1}{r_{12}} \right| \pi_1(1)\pi_2(2) \right\rangle$$

$$K\pi_1\pi_2 = \left\langle \pi_1(1)\pi_2(2) \left| \frac{1}{r_{12}} \right| \pi_2(1)\pi_1(2) \right\rangle$$

For a homonuclear diatomic molecule one can easily prove that

$$J\pi_1\pi_1 = J\pi_2\pi_2 = J\pi_1\pi_2 \tag{7.173}$$

Because the electron repulsion integrals are positive, the most stable of the three states of O_2 should be ${}^3\Sigma_g^-$. This agrees with the experimental observations and is consistent with Hund's multiplicity rule. This also explains the well known paramagnetism of oxygen gas as the ground state is a triplet state. The simple way in which the observed magnetic property of O_2 has been explained is one of the triumphs of the molecular orbital theory. The other two states of O_2 are also observed. It follows from Eqs. (7.172) that the next high energy state of O_2 above the ground state ${}^3\Sigma_g^-$ is ${}^1\Delta_g$. The ${}^1\Delta_g$ state is observed at 0.98 eV and the ${}^1\Sigma_g^+$ state at 1.63 eV above the ground state. This is also consistent with Hund's angular momentum rule which says that, of the states with same multiplicity, the one with the highest angular momentum lies lowest.

7.13 Non-crossing Rule and the Correlation Diagrams of the Homonuclear Diatomics

A complete understanding of the molecular orbitals requires us to know not only the atomic orbitals into which they dissociate when the nuclei are infinitely separated but also those into which they turn when the internuclear distance is reduced to zero, and the two nuclei coalesce. This is known as the united atom viewpoint. The atomic orbitals of the united atom together with the orbitals of the separated atoms give rise to the correlation diagram (Fig. 7.17). For example, when a proton and a hydrogen atom coalesce to form a united atom—an isoelectronic ion He^+, the $\sigma_g 1s$ orbital will pass smoothly into the helium $1s$ atomic orbital. The orbital $\sigma_u 1s$ does not, however, correlate with $2s$-orbital of helium atom since this has the wrong symmetry under inversion. In Fig. 7.12 it has been shown that $\sigma_u 1s$ orbital has a nodal plane at the centre of, and perpendicular to the bond. When the internuclear distance is reduced to zero, the two halves of $\sigma_u 1s$ orbital touch each other at the nodal plane. It is, therefore, obvious that $\sigma_u 1s$ orbital correlates with $2p$ atomic orbital of the united atom.

From a similar consideration of Fig. 7.12, the $\sigma_u 2p_x$ correlates with $2p_x$ and $\sigma_g 2p_x$ with $3d_{xy}$. It is to be noticed that among the molecular orbitals whose separated atom parentage is a 2-quantum state, all the bonding orbitals have a united atom correlation with the same principal quantum number as in the separated atoms while all the antibonding ones show an increase of quantum number by either 1 or 2 in the united atom.

There is one important point in building up the correlation diagram. How does one know that $\sigma_g 2s$ orbital correlates with $2s$ orbital and $\sigma_g 2p$ with $3s$-orbital of the united atom and not the other way round? This is due to the operation of the non-crossing rule which says that two states of the same symmetry cannot cross as the internuclear distance is varied. The proof of this theorem is due to Neumann and Wigner and later by Teller[22].

Let us consider two electronic states ϕ_1 and ϕ_2 of a diatomic molecule. When the internuclear distance is reduced, the energies of the orbitals as well as their wavefunctions change. The new orbital at a smaller value of internuclear distance may have the wavefunction of the form

$$\psi = c_1\phi_1 + c_2\phi_2 \tag{7.174}$$

where c_1 and c_2 are such that the energy given by

$$E = \frac{\langle \psi \mid H_e \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \tag{7.175}$$

is minimum. The application of the variation theorem leads to the following secular determinant

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0$$

since

$$\Delta_{11} = \Delta_{22} = 1$$
$$\Delta_{12} = 0$$

The solutions of this determinant may be written as

$$E = \frac{H_{11} + H_{22} \pm \sqrt{(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - H_{12}^2)}}{2}$$
$$= \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2}\{(H_{11} - H_{22})^2 + 4H_{12}^2\}^{1/2} \tag{7.176}$$

Corresponding to the two roots, there will be two new wavefunctions say, ψ_1 and ψ_2. If the two roots are equal at a certain value of internuclear distance, then the crossing in the correlation diagram can occur. In order that the two roots in Eq. (7.176) be equal, the conditions

$$H_{11} = H_{22} \quad \text{and} \quad H_{12} = 0 \tag{7.177}$$

must be satisfied simultaneously. If ϕ_1 and ϕ_2 have different symmetry then $H_{12} = \langle \phi_1 \mid H_e \mid \phi_2 \rangle = 0$ (since $g \times u = u$, but the nonvanishing integral must be symmetric).

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[22] E. Teller, *J. Chem. Phys.*, 41, 109, 1936.

Since H_{11} and H_{22} are functions of internuclear separation it may be possible for these two integrals to be equal at some distance. In that case, the two energy levels become equal and the crossing can occur. If ϕ_1 and ϕ_2 have same symmetry then $H_{12} \neq 0$. In general, it is not possible, by varying the internuclear distance, to satisfy the two conditions of Eq. (7.177). Hence the two energy levels given by Eq. (7.176) cannot be equal and the crossing is impossible.

It follows that the potential energy curves for states of different symmetries in a diatomic molecule can cross. This argument is equally valid for states of different spin multiplicities.

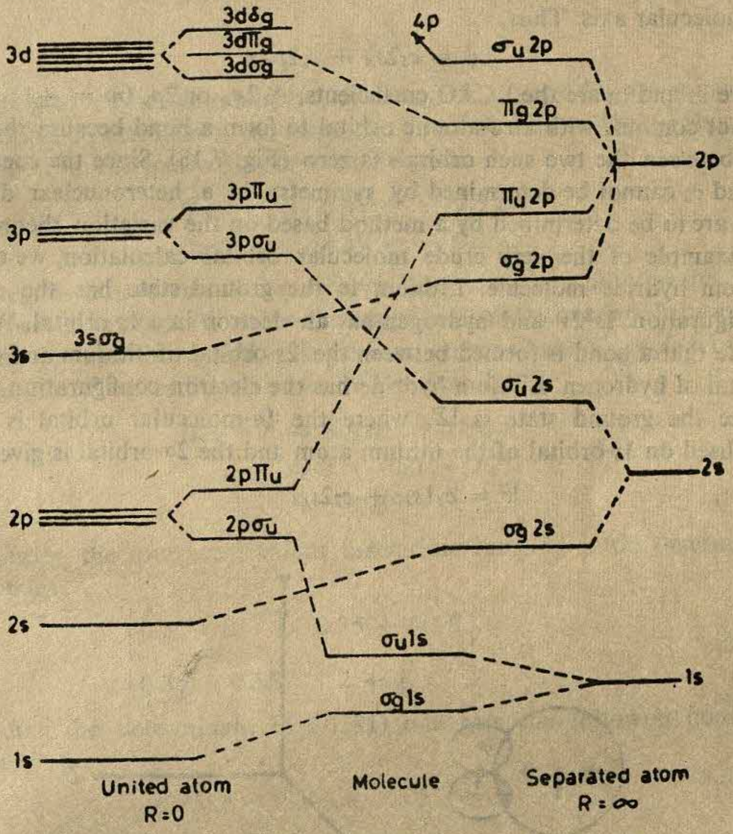

Fig. 7.17 *Correlation diagram for the homonuclear diatomics.*

7.14 Molecular Orbitals of the Heteronuclear Diatomic Molecules

The heteronuclear diatomic molecules have no centre of symmetry. Any particular molecular orbital may be compounded from atomic orbitals of different electronic shells (for example, 1*s* orbital of H and $2p_z$-orbital of F in HF), and therefore the former notations like $\sigma 1s$, $\sigma 2s$, $\sigma 2p$, $\pi 2p$, etc. cannot be always used. Mulliken used the notations like $x\sigma$, $y\sigma$, $z\sigma$, $w\pi$, $v\pi$, etc. with an advantage of applying to heteronuclear diatomics. However, these notations are very rarely used now-a-days. It is still true that the molecular orbitals are of σ, π, δ. . . . type and their degeneracy is same as in the homonuclear case. Total molecular electronic states will be represented by Σ^+, Σ^-, Π, Δ. etc.

Although two dissimilar atomic orbitals may be involved in the formation of a molecular orbital, there is no ambiguity regarding ihe value of λ for the molecular orbital. Atomic orbitals characterised by same value of m can only combine to form a molecular orbital in a heteronuclear diatomic molecule. For example, a $2s$ orbital on atom A can combine with the $2p_z$ $(m = 0)$ orbital on B to form a molecular orbital if z is chosen the direction of molecular axis. Thus,

$$\psi = c_1 2s_A + c_2 2p_{z,B}$$

where c_1 and c_2 are the LCAO coefficients. A $2p_x$ or $2p_y$ $(m = \pm 1)$ orbital cannot combine with an s-atomic orbital to form a bond because the overlap between the two such orbitals is zero (Fig. 7.18). Since the coefficients c_1 and c_2 cannot be determined by symmetry in a heteronuclear diatomic they are to be determined by a method based on the variation theorem. As an example of the very crude molecular orbital calculation, we take the lithium hydride molecule. Lithium in the ground state has the electron configuration $1s^2 2s$ and hydrogen has an electron in a $1s$ orbital. We anticipate that a bond is formed between the $2s$-orbital of lithium and the $1s$-orbital of hydrogen. Lithium hydride has the electron configuration $1\sigma^2 2\sigma^2$, hence the ground state is ${}^1\Sigma$, where the 1σ-molecular orbital is mainly localised on $1s$-orbital of the lithium atom and the 2σ-orbital is given by

$$\Psi = c_1 1s_H + c_2 2s_{Li} \tag{7.178}$$

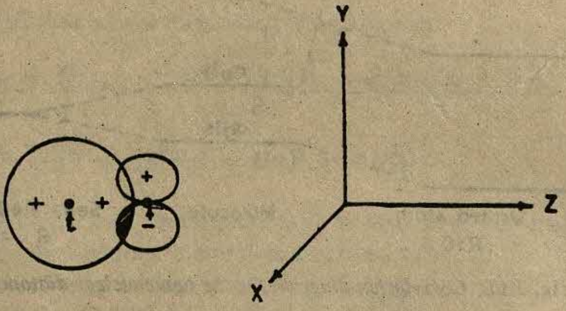

Fig. 7.18 *The overlap between an s-type orbital on one atom and p_x (or p_y) type on other atom. The positive overlap region (unshaded) is exactly cancelled by the negative overlap (shaded) region.*

Thus, we assume that lithium hydride is essentially a two-electron problem. The application of the variation method leads to the following secular determinant which is zero.

$$\begin{vmatrix} H_{11} - E & H_{12} - SE \\ H_{12} - SE & H_{22} - E \end{vmatrix} = 0$$

where

$$\begin{aligned} H_{11} &= \langle 1s_H \mid H_e \mid 1s_H \rangle \\ H_{22} &= \langle 2s_{Li} \mid H_e \mid 2s_{Li} \rangle \\ H_{12} &= \langle 1s_H \mid H_e \mid 2s_{Li} \rangle \\ S &= \langle 1s_H \mid 2s_{Li} \rangle \end{aligned} \qquad (7.179)$$

and H_e is an effective electronic hamiltonian of the molecule. At the equilibrium bond length of 3 a.u. (1.6 Å) the overlap integrals have the value

$$S = 0.5$$

According to the simple treatment, the integrals H_{11} and H_{22} are equated to the ionisation potentials of the respective atomic orbitals. Their values are available from the spectroscopic data. They are

$$\begin{aligned} H_{11} &= -13.6 \text{ eV} = -0.5 \text{ a.u.} \\ H_{22} &= -5.44 \text{ eV} = -0.2 \text{ a.u.} \end{aligned}$$

The integrals H_{12}, often called resonance integral and usually denoted by β, is assumed to be proportional to the magnitude of the overlap between the two atomic orbitals. Mulliken[23] gave an approximate formula for the evaluation of β, according to which H_{12} is given by[24]

$$\begin{aligned} H_{12} = \beta &\approx KS(H_{11} + H_{22})/2 \\ &\approx 0.5(-0.5 - 0.2) \\ &= -0.35 \end{aligned} \qquad (7.180)$$

Substituting the numerical values for various integrals in the determinant one obtains

$$\begin{vmatrix} 0.5 + E & 0.35 + 0.5E \\ 0.35 + 0.5E & 0.2 + E \end{vmatrix} = 0 \qquad (7.181)$$

Expanding the determinant in (7.181) one gets the following quadratic equation:

$$0.75E^2 + 0.35E - 0.023 = 0 \qquad (7.182)$$

Equation (7.182) has the following roots:

$$E = -0.526, +0.06$$

The lowest root (i.e. -0.526) corresponds to the energy of the lowest molecular orbital which should be occupied with two electrons in the ground state of the lithium hydride molecule. We shall now find the molecular orbital corresponding to this energy. Substituting this value of E into one of the secular equations, we obtain

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[23] R.S. Mulliken, *J. Chem. Phys.*, 46, 497; 675, 1949.

[24] The value of K for the 2s-1s atomic orbital overlap is usually taken as ~ 2.

$$C_1(0.50 - 0.526) + C_2(0.35 + 0.5 \times -0.526) = 0$$

or

$$C_1/C_2 = 3.3 \tag{7.183}$$

Let ψ_1 be the molecular orbital corresponding to the lowest root. The normalisation condition gives the following equation

$$\langle \psi_1 \mid \psi_1 \rangle = C_1^2 \langle 1s_H \mid 1s_H \rangle + C_2^2 \langle 2s_{Li} \mid 2s_{Li} \rangle + 2C_1C_2 \langle 1s_H \mid 2s_{Li} \rangle = 1$$

or

$$C_1^2 + C_2^2 + 2C_2C_1S_2 = 1 \tag{7.184}$$

since each of $1s_H$ and $2s_{Li}$ orbitals are individually normalised. Combining Eqs. (7.183) and (7.184) and using the value of S as 0.5, we get

$$C_1 = 0.8465, \qquad C_2 = 0.2565$$

Therefore, the lowest molecular orbital is given by

$$\psi_1 = 0.8465(1s_H) + 0.2565(2s_{Li}) \tag{7.185}$$

Using this wavefunction, one finds the density in the 2σ-molecular orbital of lithium hydride as

$$\begin{aligned}\rho = 2\psi_1^2 = 2[&(0.8465)^2 1s_H^2 + (0.2565)^2 2s_{Li}^2 \\ &+2\times 0.8465\times 0.2565(1s_H,\ 2s_{Li})]\end{aligned} \tag{7.186}$$

This density consists of atomic orbital densities like $1s_H^2$ and $2s_{Li}^2$ and the overlap density $1s_H 2s_{Li}$. Mulliken proposed that the overlap density like $\phi_a\phi_b$ where ϕ_a and ϕ_b are the atomic orbitals on atoms a and b could be equally divided between the orbitals ϕ_a and ϕ_b according to the following approximate formula[25]

$$\phi_a\phi_b = \frac{1}{2}S_{ab}(\phi_a^2 + \phi_b^2) \tag{7.187}$$

where S_{ab} is the overlap integral. This formula ensures the conservation of the net charge. Equation (7.186) may now be written as

$$\begin{aligned}\rho &= 2[(0.8465)^2 1s_H^2 + (0.2565)^2 2s_{Li}^2 + 0.8465\times 0.2565 \\ &\quad \times 0.5\times(1s_H^2 + 2s_{Li}^2)] \\ &= 2[(0.7166\cdot 1s_H^2 + 0.0658\cdot 2s_{Li}^2 + 0.1085(1s_H^2 + 2s_{Li}^2)] \\ &= 2[0.8251(1s_H^2) + 0.1743\cdot(2s_{Li}^2)] \\ &= 1.65\cdot(1s_H^2) + 0.35(2s_{Li}^2)\end{aligned} \tag{7.188}$$

This procedure gives what Mulliken calls the gross atomic population numbers which add up to the total number of electrons in the bond. Since the

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[25] R.S. Mulliken, *J. Chem. Phys.*, **46**, 497, 1949. This formula is valid for homonuclear diatomics but rather ambiguous in the case of heteronuclear diatomic molecules.

1σ-molecular orbital with its two electrons is localised on the lithium atom, the net electron populations on the hydrogen and lithium atoms in lithium hydride are respectively 1.65 and 2.35. This leads to the ionic character of the bond that can be described as

$$Li^{+0\cdot65} - H^{-0\cdot65}$$

These mumbers are in qualitative agreement with the observations that lithium hydride is predominantly ionic in its ground state.

We shall now examine the behaviour of lithium hydride in its lowest excited state. The molecular orbitals corresponding to the root $(+0.06)$ of Eq. (7.182) is obtained as before by substituting this value of E into a secular equation and employing the normalisation condition, one obtains

$$\psi_2 = -0.7691(1s_H) + 1.1310(2s_{Li}) \tag{7.189}$$

Therefore

$$\begin{aligned}\psi_2^2 &= (0.7691)^2(1s_H^2) + (1.131)^2(2s_{Li}^2) - 2\times 0.7691\times 1.131(1s_H 2s_{Li})\\ &= 0.5915(1s_H^2) + 1.2792(2s_{Li})^2 - 0.4349(1s_H + 2s_{Li}^2)\\ &= 0.16(1s_H)^2 + 0.84(2s_{Li})^2\end{aligned} \tag{7.190}$$

The lowest excited state is obtained by promoting an electron from ψ_1 to ψ_2 without disturbing the core electrons in 1σ. The net atomic population numbers on the hydrogen and lithium atoms in the lowest excited state of lithium hydride, are given as

$$\begin{aligned}\rho' &= \psi_1^2 + \psi_2^2 + 2(1\sigma)^2\\ &= 0.98(1s_H^2) + 3.02(2s_{Li})^2\end{aligned} \tag{7.191}$$

The lowest electronic excited state of lithium hydride may be described as

$$Li^{-0\cdot02} —— H^{+0\cdot02}$$

which demonstrates that the molecule is predominantly covalent in its lowest excited state. The numbers in Eqs. (7.188) and (7.191) are highly approximate in view of the crude nature of the calculation. However, this example illustrates qualitatively the principle used to derive the information of chemical interest from the molecular orbital theory.

7.15 Correlation Diagrams of the Heteronuclear Diatomics

We have already found three molecular orbitals of lithium hydride according to the simple treatment. They are 1σ, ψ_1 and ψ_2 where ψ_1 and ψ_2 are also the orbitals of σ-symmetry. It is obvious from Eqs. (7.185) and (7.189) that ψ_1 correlates with $1s_H$ and ψ_2 with $2s_{Li}$ when the internuclear distance increases to infinity. Figure 7.19 shows how the three orbitals of lithium hydride correlate with the orbitals of the united atom (i.e. Be) and of the separated atoms. A correlation diagram for the heteronuclear diatomic molecules similar to Fig. 7.17 can be drawn when molecular orbitals are constructed from two identical atomic orbitals, one from each atom. The most

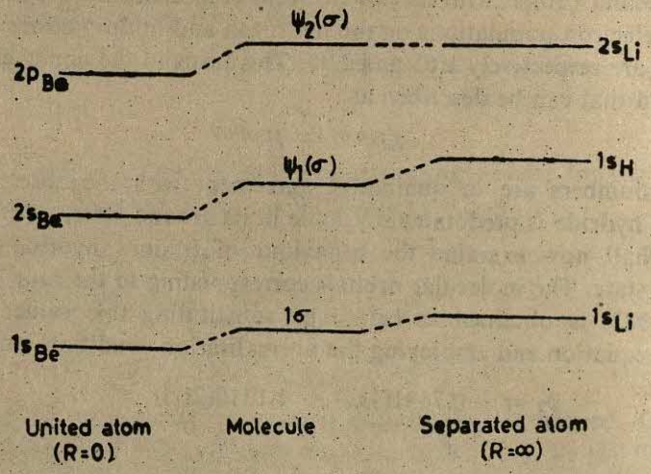

Fig. 7.19 *Correlation diagram of lithium hydride*

important difference from the correlation diagram of Fig. 7.17 is that, because of the absence of g–u symmetry, the second orbital, which for a homonuclear diatomic molecule would be σ_u 1s, correlates with the 2s orbitals of the united atom. Figure 7.20 gives the correlation diagram of a heteronuclear diatomic molecule AB with A being more electron-negative than B. The non-crossing rule is obeyed so that two σ or two π orbitals do not cross. It should be noted that because of lower symmetry for the heteronuclear diatomics there are less crossings in Fig. 7.20 than in Fig. 7.17.

7.16 Hartree-Fock Self-Consistent Field Method

The solutions of the Hartree-Fock equations, for atoms and ions have been obtained but the Hartree-Fock equations for molecules are too difficult to solve exactly. This difficulty arises from the dependence of molecular orbital functions on two or more coordinates whereas in the case of atoms angular coordinates can be separated out, as spherical harmonics and then we can work out the radial functions which depend only on a single variable, r. Roothaan[26] has developed a self-consistent field (SCF) method for molecules. In this method the molecular orbitals are constructed as before from a linear combination of atomic orbitals which may, in turn, be solutions of the Hartree-Fock equations for the respective free atoms. However, for convenience, the Slater's orbitals are very commonly used. For qualitative or semi-qualitative discussion, the exact functional form of atomic orbitals is of minor importance. Slater's atomic orbital is of the following form:

$$\phi(n, l) = Nr^{n-1} \exp(-\rho r) Y_{l,m}(\theta, \phi)$$

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[26] C.C.J. Roothaan, *Rev. Mod. Phys.*, **23**, 69, 1951.

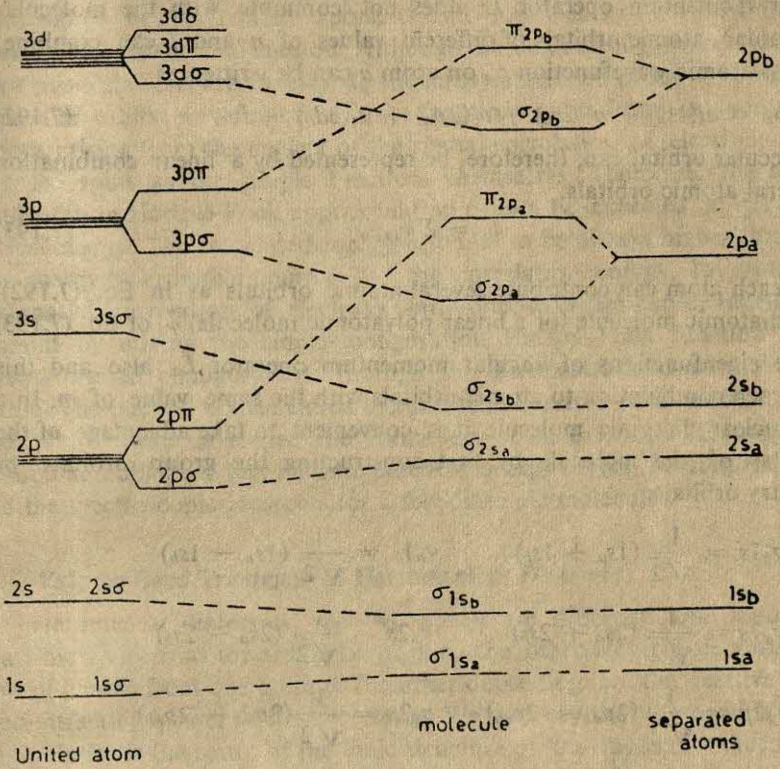

Fig. 7.20 *Correlation diagram for the heteronuclear diatomics.*

where N is a normalisation constant, n and l are principal and orbital angular momentum quantum numbers and $Y_{l,m}(\theta, \phi)$ is the angularly dependent component. The orbital exponent ρ is an effective nuclear charge that allows for the screening of atomic nucleus by other electrons in the atom. Although Slater gave a set of empirical rules for determining ρ for orbitals in free atoms, these values may not necessarily be the best values when the atomic orbitals are combined linearly to form molecular orbitals. Therefore, in an accurate calculation the ρ values for various atomic orbitals are varied until the molecular energy is minimised with respect to them.

Slater's atomic orbitals contain no inner radial nodes and do not form an orthogonal set on the atom. For example, $1s$ and $2s$ orbitals on an atom are always positive and their overlap does not vanish. It is possible to orthogonalise $2s$ orbital with respect to $1s$ orbital as

$$2s' = 2s - c(1s)$$

where the coefficient c is so chosen as to make $2s'$ orthogonal to $1s$. Therefore, a greater flexibility can be introduced into the calculation by introducing a linear combination of Slater orbitals on each atom. Since the angular momentum operator $\hat{L}^2$ does not commute with the molecular hamiltonian, atomic orbitals of different values of n and l can combine. an Thus atomic wavefunction ϕ_a on atom a can be written as

$$\phi_a = a_1(1s_a) + a_2(2s_a) + a_3(2p_a) + a_4(3d_a) + \dots \tag{7.192}$$

A molecular orbital can, therefore, be represented by a linear combination of several atomic orbitals:

$$\psi_i = \sum_p c_{ip}\phi_p \tag{7.193}$$

where each atom can contribute several atomic orbitals as in Eq. (7.192). For a diatomic molecule (or a linear polyatomic molecule) ψ_i of Eq. (7.193) are the eigenfunctions of angular momentum operator $\hat{L}_z$ also and this limits each combination to atomic orbitals with the same value of m. In a homonuclear diatomic molecule it is convenient to take advantage of the symmetry of the molecule by first constructing the group orbitals or symmetry orbitals:

$$\begin{aligned}
\sigma_g 1s &= \frac{1}{\sqrt{2}}(1s_a + 1s_b) & \sigma_u 1s &= \frac{1}{\sqrt{2}}(1s_a - 1s_b) \\
\sigma_g 2s &= \frac{1}{\sqrt{2}}(2s_a + 2s_b) & \sigma_u 2s &= \frac{1}{\sqrt{2}}(2s_a - 2s_b) \\
\sigma_g 2p &= \frac{1}{\sqrt{2}}(2p_{\sigma a} + 2p_{\sigma b}) & \sigma_u 2p &= \frac{1}{\sqrt{2}}(2p_{\sigma a} - 2p_{\sigma b}) \\
\sigma_g 3d &= \frac{1}{\sqrt{2}}(3d_{\sigma a} + 3d_{\sigma b}) & \sigma_u 3d &= \frac{1}{\sqrt{2}}(3d_{\sigma a} - 3d_{\sigma b})
\end{aligned} \tag{7.194}$$

These symmetry orbitals are essentially molecular orbitals when the internuclear distance R is very large. For smaller values of R, molecular orbitals are generally a linear combination of simple symmetry orbitals of same symmetry type. For example in Eq. (7.194) we have four symmetry orbitals of symmetry σ_g, and therefore we should have four σ_g molecular orbitals which are orthogonal to each other. They are denoted, in order of increasing orbital energy as $\psi_1(\sigma_g)$, $\psi_2(\sigma_g)$, $\psi_3(\sigma_g)$ $\psi_4(\sigma_g)$. Thus we have

$$\begin{gathered}
\psi_i(\sigma_g) = b_{i1}(\sigma_g 1s) + b_{i2}(\sigma_g 2s) + b_{i3}(\sigma_g 2p) + b_{i4}(\sigma_g 3d) \\
i = 1, 2, 3, 4
\end{gathered} \tag{7.195}$$

and similarly for $\psi_i(\sigma_u)$. Once the sequence of orbital energies is known the ground state wavefunction of a $2n$-electron system may be written in the form of a Slater determinant as

$$\psi_0 = \frac{1}{\sqrt{2n!}} \left| \bar{\psi}_1(\sigma_g)\, \psi_1(\sigma_g)\, \psi(\sigma_u)\, \bar{\psi}_1(\sigma_u) \dots \right| \tag{7.196}$$

The average energy for this ground state wavefunction is then determined by the SCF procedure where not only the orbital exponents ρ but also the coefficients b_{ij} are varied until the energy is minimum.

For any molecule the single configuration approximation with the optimum values of the orbital exponents and coefficients is just the Hartree-Fock self-consistent field method. Although the single-configuration Hartree-Fock wavefunctions are superior to the antisymmetrised product of simple molecular orbital wavefunctions, these functions suffer from the same limitations arising from the neglect of the spatial correlation of electrons with opposed spins as the simple functions themselves. Therefore, the single configuration Hartree-Fock approximation cannot be expected to give the correct energy. The calculated energy is found to be always higher than the true energy by a finite amount called the correlation energy. In principle, the spatial correlation of electrons with opposed spins can be taken into account by mixing the single-configuration Hartree-Fock function with several excited configurations through the interelectronic Coulomb interaction. The method is then called the extended Hartree-Fock method. Das and Wahl[27] have developed the formalism of the extended Hartree-Fock method and obtained very realistic potential energy curves, binding energies, and the spectroscopic constants for a few diatomic molecules.

7.17 Valence Bond Treatment of Heteronuclear Diatomics

In heteronuclear diatomics, the two atoms are different. One atom can draw more electrons toward its centre than the other atom. This results in flow of charge from one atom to the other depending on the relative electron-attracting power of the two atoms. We then say that the bond is polar and polarity is the result of the ionic structure of the molecule. According to the VB treatment of a heteronuclear diatomic AB, the best possible wavefunction could be written as

$$\psi = C_1\psi_{AB} + C_2\psi_{A^+B^-} + C_3\psi_{A^-B^+} \tag{7.197}$$

where, omitting the spin factors,

$$\begin{aligned}\psi_{AB} &= \phi_A(1)\,\phi_B(2) + \phi_A(2)\,\phi_B(1)\\ \psi_{A^+B^-} &= \phi_B(1)\,\phi_B(2)\\ \psi_{A^-B^+} &= \phi_A(1)\,\phi_A(2)\end{aligned}$$

where ϕ_A and ϕ_B are the appropriate atomic orbitals of the atoms A and B respectively. The coefficients C_1, C_2 and C_3 could be determined by the variation method. But, then, it is necessary to determine the energies of the three structures.

The energy of the ionic structure A^+B^- is given by $I_A - A_B + Q$ where I_A is the ionisation potential of atom A and A_B is the electron affinity of atom B and Q is the Coulomb attraction between the positive and negative charges, i.e. e^2/R_{AB}. Similarly, the energy of the ionic structure A^-B^+ is given by $I_B - A_A + Q$. For a homopolar bond one can assume that the two structures occur with equal weight in Eq. (7.197) and this is possible if

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[27] G. Das and A.C. Wahl, *J. Chem. Phys.*, **44**, 87, 1966.

$$I_A - A_B + Q = I_B - A_A + Q$$

i.e.

$$I_A + A_A = I_B + A_B$$

This is the definitive property of electronegativity values. Mulliken[28] adopted the mean of I and A to denote electronegativity, χ_A of an atom A as

$$\chi_A = 1/2(I_A + A_A) \tag{7.198}$$

$\chi_A > \chi_B$, then A^+B^- has higher energy than A^-B^+. Thus a scale for electronegativity of each element is evolved and the ionic character of a bond in AB is determined by $|\chi_A - \chi_B|$. The chief drawback of Mulliken's scale is that it uses isolated atom properties while electronegativity means to describe the behaviour of an atom in a molecule.

On the other hand, Pauling[10] adopted $\sqrt{\Delta}$ as a measure of the difference in electronegativities of two elements as $\sqrt{\Delta} \approx |\chi_A - \chi_B|$ where Δ is defined as $\Delta = D_{e,AB} - (D_{e,A2} \cdot D_{e,B2})^{1/2}$ with D_e being the bond dissociating energy. In Pauling's original treatment one of the ionic structures A^+B^- and A^-B^+ is unimportant from the energy considerations. Thus for the polar molecule HF, the energy of H^-F^+ is about 7 eV higher than the energy of H^+F^-. So in the ground state of HF such structure can be assumed to play no role in the bonding. Therefore, the wavefunction of HF can be written as

$$\Psi_{HF} = C_1\, \psi_{H.F}\,(\text{cov}) + C_2 \psi_{H^+F^-}\,(\text{ion}) \tag{7.199}$$

while C_1 and C_2 can be determined by the variation method. Pauling gave a simple treatment from chemical intuition. He said that the dipole moment of HF arose mainly from the ionic structure H^+F^-. Since $R_e = 0.92$ Å and the dipole moment of HF is 1.82 D, one may write

$$C_2^2 \cdot e \times R_e = 1.82\ D$$

$$C_2^2 = \frac{1.82}{4.8 \times 10^{-10} \times 0.92 \times 10^{-8}} = 0.41$$

Since $C_1^2 + C_2^2 = 1$ because Ψ_{HF} of Eq. (7.199) must be normalised by neglecting the overlap, one has $C_1^2 = 0.59$. Thus one may conclude that HF has 41% ionic character and 59% covalent character. Table 7.3 gives the values of C_2^2 for halogen hydrides. The results of Table 7.3 are reasonable. As we should expect from chemical knowledge the electronegativity difference between the hydrogen and halogen atom decreases as we go to heavier elements so the value of C_2^2 should decrease.

TABLE 7.3 IONIC CHARACTER IN THE HYDROGEN HALIDES

Molecules	*HF*	*HCl*	*HBr*	*HI*
$\mu(D)^*$	1.82	1.03	0.83	0.45
C_2^2	0.41	0.17	0.11	0.05

$(1D^* = 3.334 \times 10^{-30}\ \text{Cm})$

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[28] R.S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934) and 3,573 (1935).

This treatment of Pauling is not very accurate because it assumes that the covalent function in Eq. (7.199) does not contribute to polarity of the bond. But Coulson[29] has shown that homopolar dipole could arise from inequality of the size of the atomic orbitals. The more dissimilar the atoms are in size, larger is the homopolar dipole. The homopolar dipole in HCl is about 1*D*.

Although we have talked of ionic and covalent structures in describing a chemical bond in the VB theory, they do not really exist as separate entities. It is also inaccurate to speak of any resonance between them. The main value of the VB theory lies in its selection of a particular structure which has the largest weight in the molecular wavefunction and gives a simple pictorial description of the chemical bond.

APPENDIX 7

The two centre molecular integrals are evaluated by transforming the variables into elliptical coordinates. The transformation is as follows:

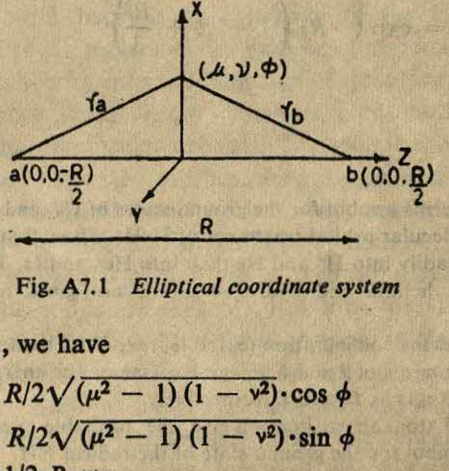

Fig. A7.1 *Elliptical coordinate system*

From Fig. A7.1, we have

$$X = R/2\sqrt{(\mu^2 - 1)(1 - \nu^2)}\cdot\cos\phi \tag{A7.1}$$

$$Y = R/2\sqrt{(\mu^2 - 1)(1 - \nu^2)}\cdot\sin\phi \tag{A7.2}$$

$$Z = 1/2\, R\cdot\mu\nu \tag{A7.3}$$

$$\mu = \frac{r_a + r_b}{R}, \quad \nu = \frac{r_a - r_b}{R} \tag{A7.4}$$

$$d\tau = \frac{R^3}{8}(\mu^2 - \nu^2)\, d\mu\, d\nu\, d\phi \tag{A7.5}$$

The range of variables is as follows

$$1 \leqslant \mu \leqslant \infty, \; -1 \leqslant \nu \leqslant +1, \; 0 \leqslant \phi \leqslant 2\pi$$

We shall here evaluate the overlap integral *S* defined by

$$S = \int 1s_a\cdot 1s_b\, d\tau \tag{A7.6}$$

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[29] C.A. Coulson, "*Valence*", Second Edition, Oxford University Press, 1961.

Using the explicit form of hydrogen 1*s*-atomic orbitals and making the transformations just described, one obtains

$$\begin{aligned} S &= \frac{1}{\pi}\int \exp\left[-(r_a + r_b)\right] d\tau \\ &= \frac{R^3}{8\pi}\int_1^{\infty} \exp(-\mu R)\, d\mu \int_{-1}^{+1} (\mu^2 - \nu^2)\, d\nu \int_0^{2\pi} d\phi \\ &= \frac{R^3}{4}\int_1^{\infty} \exp(-\mu R)\, d\mu) \left[\mu^2 \int_{-1}^{+1} d\nu - \int_{-1}^{+1} \nu^2\, d\nu\right] \\ &= \frac{R^3}{2}\int_1^{\infty} \exp(-\mu R)\, \mu^2 d\mu - \frac{R^3}{6}\int_1^{\infty} \exp(-\mu R)\, d\mu \qquad \text{(A7.7)} \end{aligned}$$

The two integrals in Eq. (A7.7) are evaluated making use of the following standard integral.

$$\int_1^{\infty} \exp(-ax)x^n\, dx = \frac{n!}{a^{n+1}}\cdot \exp(-a) \sum_{k=0}^{n} \frac{a^k}{k!} \qquad \text{(A7.8)}$$

The resulting analytic expression for S is

$$S(R) = \exp(-R)\left(1 + R + \frac{R^2}{3}\right) \qquad \text{(A7.9)}$$

PROBLEMS

1. Determine the terms symbol for the ground states of C_2^+ and B_2^+.
2. Describe the molecular orbital treatment of HeH^+. Show that the ion $HeH+$ dissociates more readily into H^+ and He than into He^+ and H. The ionisation potentials of neutral helium and hydrogen atoms are given as 24.6 eV and 13.6 eV respectively.
3. The ion He_2^+ has the configuration $(\sigma_g 1s)^2 (\sigma_u 1s)^1$. Find the total electronic energy of this system in terms of J and K integrals. Assume the energies of the molecular orbitals $\sigma_g 1s$ and $\sigma_u 1s$ as E_1 and E_2 respectively.
4. Using the united atom approximation give the probable electronic configuration and the term symbol for the ground state of the radical NH.
5. The MO wavefunction of the valence electrons in LiH is given by

   $$\psi_{MO} = 0.323\ \phi_{2s}^{Li} + 0.231\ \phi_{2p}^{Li} + 0.685\ \phi_{1s}^{H}$$

   where ϕ stands for the atomic orbital functions. Find the charge distribution of valence electrons in LiH, the extent of promotion of electrons from 2*s*-orbital to 2*p*-orbital in Li and the fractional ionic character of the bond. Assume that core electrons of Li occupy the 1*s*-orbital of Li and the overlap

   $$\langle \phi_{2s}^{Li} \mid \phi_{1s}^{H} \rangle = \langle \phi_{2p}^{Li} \mid \phi_{1s}^{H} \rangle = 0.5$$

   for the equilibrium bond length of LiH (1.6) Å.
6. The ionisation potentials of some alkali metal atoms and the electron affinities of some halogen atoms are listed below

   I (eV): 5.39 (Li) 5.14 (Na)
   E (eV): 3.50 (F) 3.60 (Cl)

   At what distances is it energetically favourable for M^+X^- to form?

8

Chemical Bonding in Polyatomic Molecules

8.1 Directed Valence: Introduction

There are two quantum-mechanical approaches to explain the chemical bonding, viz. molecular orbital theory and valence bond theory. In the molecular orbital treatment described in the previous chapter, electron pairs were delocalised over the nuclei and not concentrated just between two nuclei. Valence bond theory is an extension of the Heitler-London treatment of the hydrogen molecule and may be considered as a direct translation of the Lewis theory into the language of quantum chemistry. According to the valence bond theory electrons in a molecule occupy atomic orbitals rather than molecular orbitals. The atomic orbitals overlap on bond formation and the larger the overlap, the stronger is the bond. This localised picture of a chemical bond is, in a way, equivalent to the delocalised picture given by the molecular orbital theory because, if the charge distributions in each molecular orbital are worked out and then added up in the regions where the bonds are expected, it will be found that the total charge density will be nearly two, that is the charge on an electron pair.

But with the localised electron-pair concept, it is much easier to visualise the shape of polyatomic molecules than with the delocalised or the molecular orbital concept of electron-pair bond. The concept of directed valence is a direct consequence of this localised electron-pair (or valence bond) theory.

The essential condition for chemical bonding is that the orbitals of atoms participating in bond formation must overlap and the direction of the bond is determined by the direction in which the two orbitals overlap as much as possible. Let us illustrate it with an example of the water molecule H_2O. The central oxygen atom has the electron configuration

$$1s^2 2s^2 2p_z^2 2p_x^1 2p_y^1$$

where the $2p_x$ and $2p_y$ orbitals are available for bond formation with two $1s$-orbitals of the hydrogen H_1 and H_2. Electron pairs in the $2p_z$- and $2s$-orbitals of the valence shell are called the non-bonding or lone pairs. If we place H_1 and H_2 along the directions of $2p_x$- and $2p_y$-orbitals of O (Fig. 8.1) respectively then there is strong overlap between $1s$ orbital of H_1 and $2p_x$- and between $1s$-orbital of H_2 and $2p_y$-orbitals.

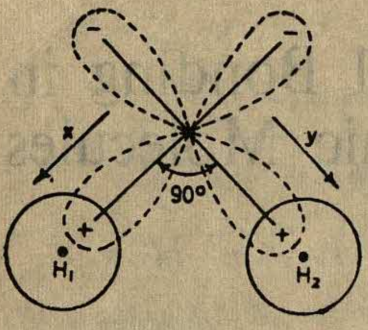


Fig. 8.1 *Localised molecular orbital of* H_2O

Thus, we can construct two localised molecular orbitals of the form

$$\phi_1 = C_1 1s(H_1) + C_2 2p_x(0)$$
$$\phi_2 = C_1 1s(H_2) + C_2 2p_y(0)$$

instead of making a linear combination of all four atomic orbitals. Since the s-type of atomic orbitals is non-directional and the p-type, directional and behave like vectors, the angle between ϕ_1 and ϕ_2 is expected to be 90°. In NH_3, the central nitrogen atom has the electron configuration

$$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$$

and the maximum overlapping with the three attached hydrogens will be obtained if they are placed along the X, Y and Z directions. The ammonia molecule should, therefore, be pyramidal in shape with apical angles of 90°. However, in both H_2O and NH_3, the observed bond angles are greater than 90° and this discrepancy is partially accounted for through the Coulomb repulsion between the attached hydrogen atoms which possess some positive charge owing to the dipole moments associated with O–H and N–H bonds.

8.2 Hybridisation

The simple concept of directed valence as described in the last section does not work when dealing with carbon compounds. The lowest state of a carbon atom has the configuration

$$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$$

which has two unpaired electrons and, therefore, the carbon atom should be bivalent with valence angle of about 90°. But the carbon atom is always tetravalent. In order to obtain the tetravalence, the atom has to be excited by promoting an electron from the $2s$-orbital to the vacant $2p_z$-orbital. The excited atom has then the following configuration

$$1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$$

The energy of such excitation in a carbon atom is not high and, therefore, it may be argued that the amount of energy gained through the formation of the extra-chemical bonds offsets any energy required to promote an electron from the 2*s*-orbital to 2*p*-orbital. But there is another difficulty. If we assume the bond formation to take place through overlap with the orbitals of other atoms then the carbon compounds will have three bonds of one kind and the fourth one of a different kind, on account of different overlapping properties of the *s*- and *p*-orbitals. But in methane (CH_4), all the four bonds are equivalent and are inclined at equal angles of 109° 28′ to each other as in a tetrahedron. The only way to obtain four equivalent bonds in carbon compounds like methane is to mix the atomic orbitals of different directional properties but having same or slightly different energies. The new orbitals that are generated from such mixing are called hybridised orbitals.

For example, there are three *p*-orbitals directed along the *X*-, *Y*- and *Z*-directions. Any linear combination of these three *p*-orbitals, i.e.

$$ap_x + bp_y + cp_z$$

where *a*, *b* and *c* are the arbitrary mixing coefficients can give rise to another *p*-orbital in shape though it will be oriented in a different direction depending on the values of *a*, *b* and *c*. Thus, any mixing of *p*-orbitals with each other does not give rise to any new orbital and nothing is gained by so doing except a new direction of its axis. Therefore, it is meaningless to talk of p^3-hybridisation. If, however, we mix a *p*-orbital, say p_x, with an *s*-orbital, the resultant orbitals look different from the component orbitals (Fig. 8.2).

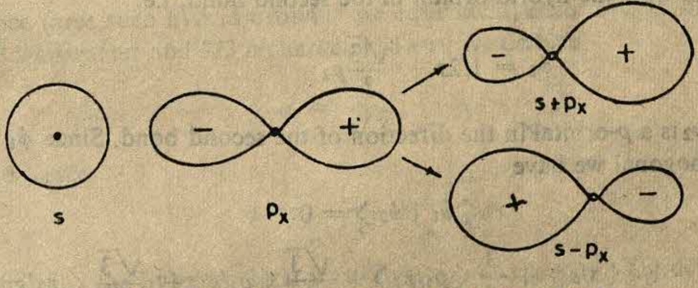


Fig. 8.2 *The boundary contours of sp-hybrid orbitals*

It should be noted that the new hybrid orbitals, called *sp*-hybrids, have more pronounced directional property than the *p*-orbitals and are expected to form stronger bonds when hydrogen atoms come up towards their positive lobes. Thus, a combination of *s*- and *p*-orbitals gives rise to new orbitals whose directional and overlapping properties are different from those of the component atomic orbitals. Such hybridisation plays an important role in describing the bonds of the carbon compounds.

Methane has four equivalent C–H bonds, which point towards the corner of a tetrahedron. We need to construct four equivalent bonds tetrahedrally oriented from one $2s$- and three $2p$-orbitals of the carbon atom. Consider a linear combination of these four orbitals, i.e.

$$\phi = as + bp_x + cp_y + dp_z \tag{8.1}$$

where $a, b, \ldots$ are the mixing coefficients. There should exist four possible combinations which are mutually orthogonal and normalised. Since the combination of three p-orbitals among themselves gives rise to another p-orbitals in any chosen direction, we assume that an appropriate combination of three p-orbitals is made and gives a p-orbital, say p_1, along the direction of the first bond. Then we write the wave function of the hybridised atomic orbital of the first bond as

$$\phi_1 = as + \lambda p_1 \tag{8.2}$$

Since four such hybrid orbitals are equivalent, each hybrid must contain the same fraction of s-character and the same fraction of p-character. We immediately deduce that each contains $1/4\,s$-character and $3/4\,p$-character. By this we mean that probability density ϕ_1^2 must contain $1/4s^2$ and $3/4p^2$. Thus, we deduce

$$a^2 = 1/4 \quad \text{or} \quad a = \tfrac{1}{2}$$

$$\lambda^2 = 3/4 \quad \text{or} \quad \lambda = \sqrt{3}/2$$

and hence

$$\phi_1 = 1/2s + \frac{\sqrt{3}}{2}p_1 \tag{8.3}$$

Consider now the hybrid orbital of the second bond, i.e.

$$\phi_2 = 1/2s + \frac{\sqrt{3}}{2}p_2 \tag{8.4}$$

where p_2 is a p-orbital in the direction of the second bond. Since ϕ_1 and ϕ_2 are orthogonal we have

$$\langle \phi_1 \mid \phi_2 \rangle = 0$$

i.e.

$$1/4 \langle s/s \rangle + \frac{3}{4} \langle p_1/p_2 \rangle + \frac{\sqrt{3}}{4} \langle p_1/s \rangle + \frac{\sqrt{3}}{4} \langle p_2/s \rangle = 0 \tag{8.5}$$

Since the net overlap between a s- and a p-orbital centred on the same nucleus is zero (Fig. 8.3), the third and fourth integrals in Eq. (8.5) vanish.

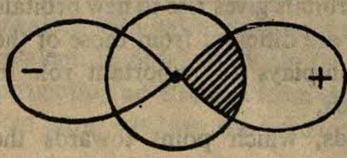


Fig. 8.3 *The overlap between a s- and a p-orbital centred on the same nucleus. The shaded and unshaded regions represent respectively the positive and negative overlaps.*

Equation (8.5) may be written as

$$1/4 + 3/4 \langle p_1 \mid p_1 \rangle \cos \theta_{12} = 0 \tag{8.6}$$

where p_2 is written as $p_1 \cos \theta_{12}$, θ_{12} being the angle between the directions of p_1- and p_2-orbitals. Thus

$$1/4 + 3/4 \cos \theta_{12} = 0$$

or

$$\cos \theta_{12} = -1/3$$

or

$$\theta_{12} = 109^\circ 28' \tag{8.7}$$

Such arguments can be extended to other bonds. Thus, sp^3-hybridisation leads to four equivalent bonds tetrahedrally oriented.

The tetrahedral hybrids are not the only hybrids that are important in carbon. There are two others, sp^2- or trigonal and sp- or diagonal hybridisations. In the trigonal hybridisation, we leave one of the three p-orbitals, say p_z, unmixed and mix s- with p_x- and p_y-orbitals. Thus we obtain three hybrid orbitals which ought to be directed in the x-y plane. Consider a linear combination of these orbitals

$$\phi' = a's + b'p_x + c'p_y \tag{8.8}$$

where a', b' and c' are the mixing coefficients.

We assume, as before, that an appropriate combination of p_x- and p_y-orbitals is made and gives a p-orbital, say p_1 along the direction of the first bond in the x-y plane. Then, we can write the wave function of the hybrid orbital of the first bond as

$$\phi_1' = a's + \lambda' p_1 \tag{8.9}$$

Since three such hybrid orbitals are equivalent, each hybrid must contain 1/3 s-character and 2/3 p-character. Thus, we deduce

$$a' = \frac{1}{\sqrt{3}}, \qquad \lambda' = \sqrt{\frac{2}{3}}$$

and hence

$$\phi_1' = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_1 \tag{8.10}$$

Similarly, the hybrid orbital wave function of the second bond is

$$\phi_2' = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_2 \tag{8.11}$$

where p_2 is a p-orbital in the direction of the second bond. Since ϕ_1' and ϕ_2' are orthogonal we have

$$\langle \phi_1' \mid \phi_2' \rangle = 0$$

or $\frac{1}{3}\langle s/s \rangle + \frac{2}{3}\langle p_1/p_1 \rangle \cos \theta_{12} + \sqrt{2/3}\,[\langle s/p_1 \rangle + \langle s/p_2 \rangle] = 0$

or

$$\frac{1}{3} + \frac{2}{3}\cos \theta_{12} = 0$$

or
$$\theta_{12} = 120^\circ \tag{8.12}$$

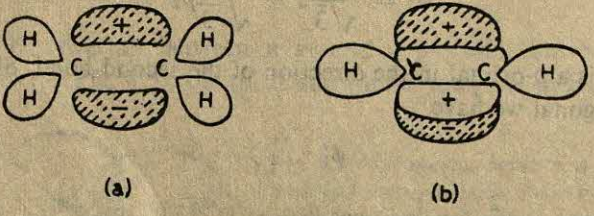
Thus three hybrid bonds in sp^2 hybridisation are inclined to each other by 120° in the x-y plane. In diagonal or sp-hybridisation, two of the three p-orbitals remain unmixed and only one p-orbital mixed with an s-orbital. The analytical expressions for the two sp-hybridised orbitals are

$$\phi_1'' = \frac{1}{\sqrt{2}}(s + p_1)$$

$$\phi_2'' = \frac{1}{\sqrt{2}}(s + p_2) \tag{8.13}$$

The orthogonality condition between ϕ_1'' and ϕ_2'' leads to a bond angle of 180°.

In olefins and aromatic hydrocarbons a carbon atom is joined to three other atoms which lie in the same plane with angles of nearly 120° at the carbon atom. In these compounds, each carbon atom is hybridised trigonally to form three equivalent bonds which are referred to as σ-bonds. Thus, in ethylene, two carbon atoms form six σ-bonds and there remains one unmixed p_z-atomic orbital associated with each carbon atom. The two p_z-orbitals, perpendicular to the plane containing σ-bonds must overlap sidewise to form a bond, called π-bond [Fig. 8.4(a)]. Thus, a double bond in any unsaturated carbon compound consists of a σ-bond and a π-bond. It is clear that the σ-electrons are contained in the plane containing the nuclei while the π-electrons are to be found in a plane perpendicular to the molecular plane. This description of a double bond explains the absence of free rotation around the bond. The diagonal hybrids explain the triple bond found in acetylene. Thus, acetylene is a linear molecule (HC = CH), and about each carbon atom, the first bond of the triple bond (i.e. σ-bond) and a carbon-hydrogen bond are formed using ϕ_1'' and ϕ_2'' of Eq. (8.13). The second and third bonds (i.e. π-bonds) of the triple bond are formed using the unmixed p_z- and p_y-orbitals associated with each carbon atom. Two π-bonds of a triple bond are, therefore, perpendicular to each other and perpendicular to σ-bond [Fig. 8.4(b)].



(a) (b)

Fig. 8.4 (a) *Shapes of the orbitals involved in the formation of the double bond in ethylene*, (b) *Shapes of the orbitals involved in the formation of the triple bond in acetylene*

When *d*-orbitals are available for hybridisation besides *s*- and *p*-orbitals, square and octahedral arrangements are formed. In a square arrangements the four equivalent orbitals are obtained from the dsp^2 combination of orbitals. The explicit analytical expressions for the four hybrid orbitals in *x-y* plane are as follows:

$$\phi_1 = \frac{1}{2}s + \frac{1}{\sqrt{2}}p_x + \frac{1}{2}\,dx^2 - y^2$$

$$\phi_2 = \frac{1}{2}s + \frac{1}{\sqrt{2}}p_y - \frac{1}{2}\,dx^2 - y^2$$

$$\phi_3 = \frac{1}{2}s - \frac{1}{\sqrt{2}}p_x + \frac{1}{2}dx^2 - y^2 \qquad (8.14)$$

$$\phi_4 = \frac{1}{2}s - \frac{1}{\sqrt{2}}p_y - \frac{1}{2}\,dx^2 - y^2$$

These mutually orthogonal hybrid-orbitals are used in a square planar complex such as $Ni(CN)_4^{=}$. The octahedral hybridisation arises from the selection d^2sp^3. These hybridised orbitals are used in octahedral complexes such as $Fe(CN)_6^{-4}$, $CO(NH_3)_6^{+3}$, etc.

8.3 Hybridisation and Geometry

It should be noted that the concept of hybridisation is a description rather than an explanation of the molecular structure or shape. However, this localised picture which the concept of hybridisation leads to, emphasises the presence of two electrons in each chemical bond and permits the shape of molecules to be easily ascertained. Lennard-Jones and Pople[1] (1950) pointed out that water and ammonia could be described in terms of sp^3-hybrid orbitals, on the central atom, which are occupied by two bonding and two lone pairs of electrons in water and three bonding and one lone pair in ammonia. Gillespie and Nyholm[2] (1957) have shown that these ideas can be extended to account for the general shapes and bond angles of most inorganic molecules. They pointed out that the arrangement of electron pairs in a valence shell of the central atom in a molecule could be regarded as arising from the mutual interactions between the electron pairs. These interactions are a consequence of both electrostatic forces and the operation of the Pauli exclusion principle. The repulsion between the electron pairs in the valence shell may be called Van der Waal's repulsion or exchange repulsion and it increases as the overlap of orbitals, each containing electron pairs, increases. Since lone pair electrons are under the influence of only one nucleus while bonding pairs are under the influence of two nuclei, orbitals containing lone pair electrons are likely to be bigger than a bonding orbital in the neighbourhood of a central atom. Hence, the lone pair orbital will overlap with the neighbouring orbitals more extensively and will repel electrons in the neighbouring orbitals more strongly than an electron pair in a bonding orbital. Thus, electron pairs in a valence shell repel each other in the following order:

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[1] J.E. Lennard Jones and J.A. Pople, *Proc. Roy. Soc.*, **A202**, 166, 1950.

[2] R.J. Gillispie and R.S. Nyholm, *Quarterly Revs.*, **339**, 1957.

lone pair-lone pair $>$ lone pair-bond pair $>$ bond pair-bond pair

In the series, CH_4, NH_3 and H_2O the successive replacement of bonding pairs by lone pairs causes the bond angle to decrease from 109.5° in CH_4 to 107.3° in NH_3 and to 104.5° in H_2O.

8.4 Simple Huckel Theory of the Linear Conjugated Systems

The unsaturated carbon compounds which consist of alternate double and single bonds are conventionally called the conjugated molecules. These molecules are generally planar, and it is taken for granted that the valence orbitals of carbon hybridise in the sp^2 manner pointing the three hybrid orbitals in the direction of three neighbouring atoms in the plane while the unhybridised $2p_z$-orbital lies with its axis perpendicular to the molecular plane. The electrons in the sp^2-orbitals, called σ-electrons, are contained in the molecular plane and do not possess any angular momentum. The orbitals formed from the unhybridised $2p_z$-orbitals are called π-orbitals and electrons in these orbitals lie above and below the molecular plane. These electrons possess one unit of angular momentum about the carbon–carbon bond. Since σ- and π-electrons are contained in planes perpendicular to each other, the interaction between these two types of electrons is likely to be negligible in the planar conjugated molecules. Therefore, the molecular orbitals for π-electrons in a conjugated system may be treated independently of σ-electrons. These orbitals are set up according to the linear combination of $2p_z$-atomic orbitals of each carbon atom in a conjugated molecule. This concept was originally introduced by Hückel[3] in 1931 but it was later developed by Coulson and Longuet-Higgins[4] and several others into a more useful theory capable of providing significant interpretations of the chemistry of such systems.

Let us consider a system of unsaturated hydrocarbons with alternate single and double bonds. If this system has n-carbon atoms each offering one $2p_z$-orbital with one π-electron in it then, according to the LCAO approximation, the molecular orbital is written as

$$\psi = \sum_i C_i \phi_i \tag{8.15}$$

where ϕ_i is a $2p_z$-atomic orbital of atom i and the summation is over all $2p_z$ atomic orbitals. The coefficients and energies of these orbitals are obtained by solving the secular equations:

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[3] E. Hückel, *Z. Physik*, **70**, 204, 1931.

[4] C.A. Coulson and H.C. Longuer-Higgins, *Proc. R. Soc.*, **192A**, 16, 1947.

$$\sum_{i=1}^{n} C_i(H_{ij} - S_{ij}E) = 0 \tag{8.16}$$

$$j = 1, 2, 3, \ldots, n$$

where

$$H_{ij} = \langle \phi_i \mid H \mid \phi_j \rangle$$

$$S_{ij} = \langle \phi_i \mid \phi_j \rangle \tag{8.17}$$

The set of secular equations (8.16) are obtained according to the variation principle described in Sec. 7.3 of the previous chapter.

Huckel introduced a set of approximations which are as follows:

1. The hamiltonian H is the sum of effective one-electron hamiltonian where the potential of each electron is determined by its own coordinates alone. Since such an effective hamiltonian in a many-electron system cannot be defined explicitly, their matrix elements are related to the empirical quantities.
2. The terms $H_{ii}(= \langle \phi_i \mid H \mid \phi_i \rangle)$, called Coulomb integral, represents approximately the energy of an electron in a $2p$-orbital on the i^{th} carbon atom. Since we are dealing with carbon atoms only, all such integrals are equal and denoted by the symbol α.
3. The terms H_{ij} $(= \langle \phi_i \mid H \mid \phi_j \rangle)$, called resonance integrals, represent the energy of interaction of two atomic orbitals. For atoms i and j not being directly bonded $H_{ij} = 0$. When atoms i and j are bonded, H_{ij} is finite. All such integrals are assumed equal and denoted by the symbol β.
4. The integrals $S_{ii} = 1$, because they are the normalisation integrals. The overlap integrals S_{ij} are neglected.

After the introduction of these approximations into the secular equations (8.16), we obtain for a linear polyene the following set of equations:

$$\begin{aligned} C_1(\alpha - E) + C_2\beta &= 0 \\ C_1\beta + C_2(\alpha - E) + C_3\beta &= 0 \\ C_2\beta + C_3(\alpha - E) + C_4\beta &= 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots & \end{aligned} \tag{8.18}$$

The corresponding determinant vanishes if the above set of equations is to have non-trivial solutions:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0\ldots \\ \beta & \alpha - E & \beta & 0 & 0\ldots \\ 0 & \beta & \alpha - E & \beta & 0\ldots \\ 0 & 0 & \beta & \alpha - E & \beta\ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{8.19}$$

If we write

$$\frac{\alpha - E}{\beta} = x \tag{8.20}$$

then Eq. (8.19) can be written as

$$\begin{vmatrix} x & 1 & 0 & 0 & 0\ldots \\ 1 & x & 1 & 0 & 0\ldots \\ 0 & 1 & x & 1 & 0\ldots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0 \tag{8.21}$$

Expansion of an $n \times n$ determinant like (8.21) yields a polynomial equation which has n real roots. Hence the system has n energy levels. The energy of the p^{th} level is given by

$$E_p = \alpha + x_p\beta \tag{8.22}$$

where x_p is the p^{th} root of the polynomial. Since α and β are negative, a positive value of x_p represents an energy level which is more negative and, therefore, more stable than the energy of an electron in a carbon $2p$-orbital. Such an energy level is called bonding molecular orbital. A negative value of x_p corresponds to a level which has higher energy and therefore less stability than an electron in a carbon $2p$-orbital. This level is called anti-bonding molecular orbital. The energy level corresponding to x_p being zero is called non-bonding molecular orbital.

Substitution of the n values of energies individually into Eq. (8.18) gives n sets of n simultaneous equations. Combining these equations with the normalisation condition for each molecular orbital yields the values of the coefficients C_1, C_2, C_3 . . . etc. for each molecular orbital. There are n-molecular orbitals for a conjugated system of n-carbon atoms. If there are n π-electrons in a system, electrons gradually fill up the orbitals starting from that of lowest energy because each orbital cannot accommodate more than two electrons. We shall illustrate this procedure with specific examples later. Now, we shall define a few quantities of chemical interest which can be derived from the simple Hückel theory.

Electron densities—For an electron in the j^{th} molecular orbital, i.e. ψ_j, the density distribution is given by ψ_j^2. The LCAO form of ψ_j is given as

$$\psi_j = \sum_i C_{ij}\phi_i \tag{8.23}$$

The normalisation condition of ψ_j gives

$$\langle \psi_j \mid \psi_j \rangle = 1$$

i.e.,

$$\langle \sum_i^n C_{ij}\phi_i \mid \sum_i^n C_{ij}\phi_i \rangle = 1$$

or

$$C_{1j}^2 \langle \phi_1 \mid \phi_1 \rangle + C_{2j}^2 \langle \phi_2 \mid \phi_2 \rangle + C_{3j}^2 \langle \phi_3 \mid \phi_3 \rangle$$
$$+ \ldots C_{nj}^2 \langle \phi_n \mid \phi_n \rangle + 2C_{1j}C_{2j} \langle \phi_1 \mid \phi_2 \rangle$$
$$+ 2C_{1j}C_{3j} \langle \phi_1 \mid \phi_3 \rangle + \ldots = 1 \qquad 8.24)$$

Integrals like $\langle \phi_i \mid \phi_i \rangle$ are normalisation integrals and are equal to unity. Since the overlap integrals $\langle \phi_i \mid \phi_j \rangle$ etc. are neglected in Hückel theory, Eq. (8.24) may be rewritten as

$$\langle \psi_j \mid \psi_j \rangle = C_{1j}^2 + C_{2j}^2 + C_{3j}^2 + \ldots C_{nj}^2$$

$$= \sum_i^n C_{ij}^2 = 1 \qquad (8.25)$$

Hence, c_{ij}^2 may be interpreted as the partial electron density on atom i due to an electron in ψ_j. The total electron density q_i at an atom i, is therefore the sum of such contributions from each electron in each molecular orbital

$$q_i = \sum_j^{\text{Occ.MOs}} n_j C_{ij}^2 \qquad (8.26)$$

when n_j is the number of electrons in the j^{th} molecular orbital and the summation in Eq. (8.26) is over all the occupied molecular orbitals. A useful check on calculations of these numbers is the knowledge that the sum of all q values equals the total number of π-electrons in the conjugated system.

Bond order--The concept of mobile bond order was introduced by Coulson (1939).[5] The partial bond order between atoms k and l in the j^{th} molecular orbital is defined as

$$p_{kl}^j = c_{kj} c_{lj} \qquad (8.27)$$

This quantity might be associated with the binding power of a π-bond. When the product of atomic coefficients is large and the coefficients are of like sign, the situation corresponds to a strong bond. If the coefficients are of opposite sign, indicative of a node between the atoms, we then have an antibonding situation. If one of the coefficients is zero, the situation then refers to a non-bonding one. The total mobile bond order or simply bond order is made up of contributions from all occupied molecular orbitals and is defined as

$$p_{kl} = \sum_j^{\text{Occ.MOs}} n_j p_{kl}^j = \sum_j^{\text{Occ.MOs}} n_j C_{kj} C_{lj} \qquad (8.28)$$

where n_j is the number of electrons in the j^{th} molecular orbital.

It is reasonable to suppose that there should be some relationships between bond order and bond length. The larger the bond order, the stronger is the bond and shorter the bond length. Therefore it is possible to find a qualitative correlation between bond order and bond length. If we assume a C–C σ-bond in ethane to have a bond order of unity, a C–C double bond in ethylene to have a bond order of two and a C–C triple bond in acetylene three, they can be shown as follows:

Molecule	*Bond length* (Å)	*Bond order*
Ethane (C − C)	1.54	1
Ethylene (C = C)	1.35	2
Acetylene (C ≡ C)	1.20	3

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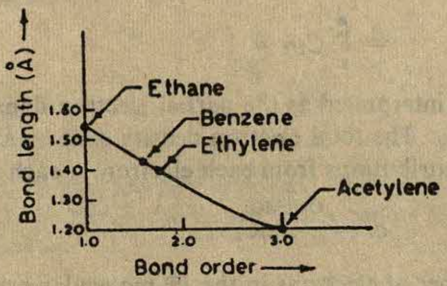
[5] C.A. Coulson, *Proc. R. Soc.*, **169A**, 413, 1939.

If these bond orders are plotted against the corresponding bond length, the order length curve (Fig. 8.5) is obtained. This curve may be utilised to predict approximate bond length for bond orders of intermediate values in conjugated hydrocarbons.

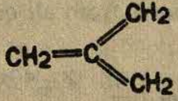


Fig, 8.5 *Bond order length curve (From "Valence", C.A. Coulson, Oxford University Press, 1952; with permissions from both author and Clarendon Press, Walton Street, Oxford)*

Free valence—The concept of free valence, F, was also introduced by Coulson.[6] It is defined as the difference between the maximum bond orders, $N_{\max}$ around a carbon atom and the total calculated bond orders N_i around the atom i in a molecule, i.e.

$$F_i = N_{\max} - N_i \tag{8.29}$$

The maximum value of N so far found in the unsaturated carbon compounds is 4.732 which is associated with the central atom of trimethylene methane:



Therefore, the free valence of a carbon atom in a molecule is given as

$$F_i = 4.732 - N_i \tag{8.30}$$

The concept of free valence provides the quantum mechanical interpretation of Thiele's theory of partial valency used in classical organic chemistry. The magnitude of free valence at a given position in a molecule determines the extent of susceptibility of that position to attack by free radicals.

8.5 Examples of Simple Huckel Calculations

Ethylene: $\overset{1}{\text{O}}\text{—}\overset{2}{\text{O}}$. This is a simple system containing two *p*-orbitals.

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[6] C.A. Coulson, *Discuss. Faraday Soc.*, 2, 9, 1947.

The determinantal form of the secular equation is simply

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

following the notations and approximations used in (8.21). The expansion of this determinant gives an equation

$$x^2 - 1 = 0$$

or

$$x = \pm 1 \tag{8.31}$$

In other words,

$$\left.\begin{aligned} E_1 &= \alpha + \beta \text{ (bonding)} \\ E_2 &= \alpha - \beta \text{ (antibonding)} \end{aligned}\right\} \tag{8.32}$$

Two available π-electrons in ethylene occupy the molecular orbital of energy $\alpha + \beta$. The total π-energy, $E\pi$ is equal to $2\alpha + 2\beta$. Since the energy of two electrons in isolated carbon $2p$-orbitals is 2α, the π-bond energy in ethylene is 2β. The coefficients of atomic orbital in each molecular orbital are obtained after substituting the values of x in any one of the two secular equations:

$$\begin{aligned} c_1 x + c_2 &= 0 \\ c_1 + c_2 x &= 0 \end{aligned} \tag{8.33}$$

For

$$x = 1$$

$$c_1 + c_2 = 0 \quad \text{or} \quad c_1 = -c_2 \tag{8.34}$$

Since every molecular orbital is normalised, the normalisation of the molecular orbital

$$\psi = c_1\phi_1 + c_2\phi_2$$

gives rise to an equation

$$c_1^2 \langle \phi_1 \mid \phi_1 \rangle + c_2^2 \langle \phi_2 \mid \phi_2 \rangle + 2c_1c_2 \langle \phi_1 \mid \phi_2 \rangle = 1$$

or

$$c_1^2 + c_2^2 = 1 \tag{8.35}$$

where the overlap integral is neglected. Combining Eqs. (8.34) and (8.35) we get

$$c_1 = \frac{1}{\sqrt{2}}, \quad c_2 = -\frac{1}{\sqrt{2}}$$

Hence, the molecular orbital which corresponds to the energy level $E_2 = \alpha - \beta$, is given by

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \tag{8.36}$$

By a similar procedure, the molecular orbital whose energy is $E_1 (E_1 = \alpha + \beta)$ is given by

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \tag{8.37}$$

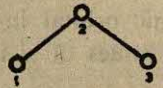
Since two π-electrons occupy the molecular orbital ψ_1 in ground state, the π-electron densities and bond order, following their definitions in Eqs. (8.26) and (8.28), are given as

$$\begin{aligned} q_1 &= q_2 = 1 \\ p_{12} &= 1 \end{aligned} \tag{8.38}$$

In ethylene each carbon atom is bonded to two hydrogen atoms. If we assign a bond order of unity to each carbon-hydrogen bond then the total bond order number N associated with each carbon atom in ethylene is four. Following the definition of free valence in Eq. (8.30) we have

$$F_1 = F_2 = 0.732 \tag{8.39}$$

Allyl system



This system contains three $2p$-carbon orbitals in a chain. The determinantal form of the secular equation is

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

Expansion of this determinant gives a polynomial

$$x^3 - 2x = 0 \tag{8.40}$$

having roots:

$$x = 0, \pm\sqrt{2} \tag{8.41}$$

The energy levels are given by

$$\begin{aligned} E_1 &= \alpha + \sqrt{2}\beta \quad \text{(bonding)} \\ E_2 &= \alpha \quad \text{(non-bonding)} \\ E_3 &= \alpha - \sqrt{2}\beta \quad \text{(antibonding)} \end{aligned} \tag{8.42}$$

The total π-electron energies of the radical, cation and anion are respectively given by

$$\begin{aligned} E_\pi \text{ (radical)} &= 3\alpha + 2\sqrt{2}\beta \\ E_\pi \text{ (cation)} &= 2\alpha + 2\sqrt{2}\beta \\ E_\pi \text{ (anion)} &= 4\alpha + 2\sqrt{2}\beta \end{aligned} \tag{8.43}$$

The three molecular orbitals corresponding to the three different roots in Eq. (8.41) are obtained after substituting the values of x in any two of the following secular equations

$$\begin{aligned} c_1x + c_2 &= 0 \\ c_1 + c_2x + c_3 &= 0 \\ c_2 + c_3x &= 0 \end{aligned} \tag{8.44}$$

For $x = -\sqrt{2}$, we have

$$\left.\begin{aligned} -\sqrt{2}c_1 + c_2 &= 0 \\ c_1 - \sqrt{2}c_2 + c_3 &= 0 \\ c_2 - \sqrt{2}c_3 &= 0 \end{aligned}\right\} \tag{8.45}$$

One of these three equations is redundant as this does not give any new relation between c_1, c_2 and c_3. Therefore, to solve for c_1, c_2 and c_3, one more equation is needed. The normalisation condition gives an equation viz.

$$c_1^2 + c_2^2 + c_3^2 = 1 \tag{8.46}$$

The combination of Eqs. (8.45) and (8.46) gives

$$c_1 = c_3 = \tfrac{1}{2}, \qquad c_2 = \frac{1}{\sqrt{2}}$$

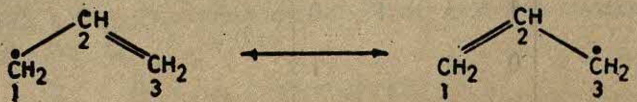
Thus the molecular orbital corresponding to the root $x = -\sqrt{2}$ (or $E_1 = \alpha + \sqrt{2}\beta$) is given by

$$\psi_1 = \tfrac{1}{2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3) \tag{8.47}$$

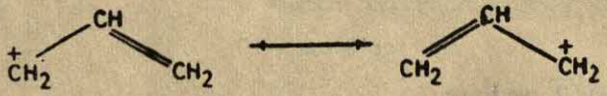
By a similar procedure, the other two molecular orbitals are obtained. They are

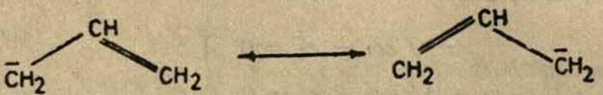
$$\left.\begin{aligned} \psi_2 &= \frac{1}{\sqrt{2}}(\phi_1 - \phi_3) \\ \psi_3 &= \tfrac{1}{2}(\phi_1 - \sqrt{2}\phi_2 + \phi_3) \end{aligned}\right\} \tag{8.48}$$

In the ground state of allyl radical, two π-electrons occupy the molecular orbital ψ_1 and the odd electron occupies the molecular orbital ψ_2. Thus, the odd electron has an equal probability of being found on carbon atoms 1 and 3 with zero probability on the middle carbon atom (i.e. atom 2). This result is in agreement with the following resonating structures of allyl radical.



where the position of the odd electron is indicated by a dot. This argument can be extended to a cation and an anion where the hole in one case or an extra electron in the other case has the same probability distribution as the odd electron in the radical. Thus we have the following resonating structures for cation and anion.





The calculations of electron densities, bond order and free valence are now straight forward. For the allyl radical which has the electron configuration $\psi_1^2\psi_2^1$, we have

$$q_1 = q_3 = 2\times\tfrac{1}{4} + 1\times\tfrac{1}{2} = 1$$

$$q_2 = 2\times 2/4 + 1\times 0 = 1$$

$$p_{12} = p_{23} = 2\times\frac{1}{2}\times\frac{\sqrt{2}}{2} + 1\times\frac{1}{\sqrt{2}}\times 0 = \frac{1}{\sqrt{2}} = 0.708$$

$$F_1 = F_3 = 4.732 - 3.707 = 1.025,$$

$$F_2 = 4.732 - (3 + 2\times 0.707) = 0.318$$

for the allyl cation which has the electron configuration $\psi_1^2\psi_2^0$, we have

$$q_1 = q_3 = 0.5; \qquad q_2 = 1.0$$

$$p_{12} = p_{23} = 0.707$$

$$F_1 = F_3 = 1.025, \qquad F_2 = 0.318$$

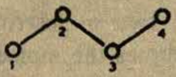
For the allyl anion with electron configuration $\psi_1^2\psi_2^2$, we have

$$q_1 = q_3 = 1.5; \qquad q_2 = 1.0$$

$$p_{12} = p_{23} = 0.707$$

$$F_1 = F_3 = 1.025, \qquad F_2 = 0.318$$

Butadiene



This system consists of four carbon $2p$-orbitals in a chain. The determinantal form of the secular equation is

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

Expansion of this determinant gives the following polynomial

$$x^4 - 3x^2 + 1 = 0 \tag{8.49}$$

with the following roots:

$$x = \pm 1.618, \pm 0.618 \tag{8.50}$$

We, therefore, have the following energy levels:

$$\begin{aligned} E_1 &= \alpha + 1.618\beta \text{ (bonding)} \\ E_2 &= \alpha + 0.618\beta \text{ (bonding)} \\ E_3 &= \alpha - 0.618\beta \text{(antibonding)} \\ E_4 &= \alpha - 1.618\beta \text{ (antibonding)} \end{aligned} \tag{8.51}$$

The total π-electron energy of the four π-electrons in butadiene is $4\alpha + 4.472\beta$. The energy of two π-electrons in ethylene is $2\alpha + 2\beta$. The delocalisation energy is defined as the difference in energy of the π-electrons in a molecule and sum of the energies of the isolated double bonds present in the classical structure of the same molecule. Butadiene has the following classical structure

$$CH_2 = CH - CH = CH_2$$

with two double bonds. Delocalisation energy (DE) is therefore given by

$$DE = 4\alpha + 4.472\beta - 2[2\alpha + 2\beta] = 0.472\beta \tag{8.52}$$

The DE is a measure of the stability of the molecule. The higher the energy, the more stable is the molecule. Thus butadiene is more stable than two ethylene molecules by an energy of 0.472β.

The four molecular orbitals are obtained by the usual procedure. In the order of increasing energy they are as follows:

$$\left.\begin{aligned} \psi_1 &= 0.3755(\phi_1 + \phi_4) + 0.6070(\phi_2 + \phi_3) \\ \psi_2 &= 0.6070(\phi_1 - \phi_4) + 0.3755(\phi_2 - \phi_3) \\ \psi_3 &= 0.6070(\phi_1 + \phi_4) - 0.3755(\phi_2 + \phi_3) \\ \psi_4 &= 0.3755(\phi_1 - \phi_4) - 0.6070(\phi_2 - \phi_3) \end{aligned}\right\} \tag{8.53}$$

The schematic diagram of these four molecular orbitals is shown in Fig. 8.6. The π-molecular orbitals always have the molecular plane as the nodal plane. Besides this, there are nodal planes perpendicular to the molecular plane. These are shown by the dotted lines in Fig. 8.6. As expected, the number of such nodal planes increases with energy in butadiene.

The calculation of electron densities, bond order and free valence leads to the following results:

$$q_1 = q_2 = q_3 = q_4 = 1$$

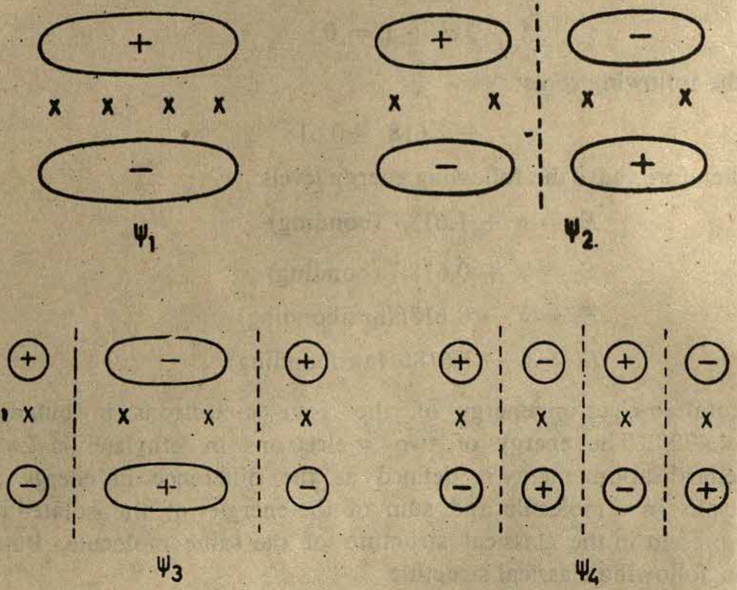
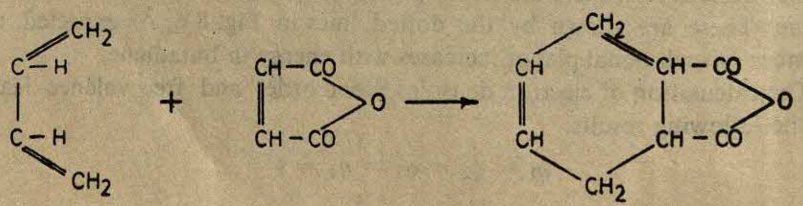


Fig. 8.6 *Schematic diagram of the four π-molecular orbitals in butadiene*

$$p_{12} = p_{34} = 0.912$$
$$p_{23} = 0.436$$
$$F_1 = F_4 = 0.820$$
$$F_2 = F_3 = 0.384$$

It is interesting to note that whilst the charge distribution in the ground state is uniform over the four atoms, the bond order between them is not. The central bond in butadiene has lower bond order than the two end bonds. This is an indication that the middle bond is weaker and longer than the two end bonds. This suggests that the assumption of the same resonance integral for all bonds in butadiene must be in error.

The free valence index shows that the central carbon atoms (i.e. atoms 2 and 3) have less partial valency than the end atoms (i.e. atoms 1 and 4) and therefore, the end atoms are more susceptible to chemical reaction than the central atoms. The 1 : 4 addition in Diels-Alder reaction can be explained from the large free valences at the end carbon atoms in butadiene.



8.6 Simple Huckel Theory for the Cyclic Conjugated Systems and Aromaticity

The classical explanation of the stability of aromatic compounds had been based on the 'strain theory'. A six-membered ring is highly stable because it undergoes no strain force. However, on the basis of this argument we cannot understand the reason why some five-membered rings such as furan and pyrrole are stable and aromatic while others such as cyclopentadiene is not. Some seven-membered conjugated rings such as tropone and tropolone are known to exist in stable form. This seems to suggest that in order to explain the aromatic stability in ring compounds, factors other than the strain forces are important.

It is difficult to give a definition of aromaticity. But this term usually applies to the mono or polycyclic conjugated systems with the following properties:

1. Molecules have planar cyclic structure.
2. Molecules show high electronic stability even if the large strain in the ring does not permit it to be stable in the classical sense.
3. Molecules exhibit characteristic chemical reactivity, such as substitution reactions.
4. Molecules show peculiarity in physical properties such as large diamagnetic susceptibility, large chemical shift in proton magnetic resonance spectra, etc.

Hückel[7] in his pioneering work gave a reasonably satisfactory explanation for aromaticity in cyclic polyenes. In a cyclic polyene one of the secular equations [see Eqs. (8.18) and (8.20)] is

$$C_{r-1} + xC_r + C_{r+1} = 0 \tag{8.54}$$

where $r - 1$, r and $r + 1$ are the successive atoms in a ring of the carbon atoms. If there are N carbon atoms in a ring, any solution must satisfy the boundary condition, i.e.

$$C_r = C_{N+r} \tag{8.55}$$

We now seek a solution which is periodic in N. We try the following:

$$C_r = e^{ir\theta} \tag{8.56}$$

Then $$e^{ir\theta} = e^{i(r+N)\theta}$$

or $$e^{iN\theta} = 1, \quad \text{i.e.} \cos N\theta + i \sin N\theta = 1 \tag{8.57}$$

$$N\theta = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi, \pm 8\pi \text{ (because } \cos(-\theta) = \cos\theta)$$

or $$\theta = 2j\pi/N, \quad \text{where } j = 0, \pm 1, \pm 2, \pm 3, \pm 4, \text{etc.} \tag{8.58}$$

If we substitute from (8.55) and (8.56) in Eq. (8.54), we obtain

$$e^{i(r-1)\theta} + xe^{ir\theta} + e^{i(r+1)\theta} = 0$$

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[7] E. Hückel, *International Conference on Physics*, London, 1934, Vol. II. The Physical Society, London, 1935, p. 9.

or
$$
\begin{aligned}
e^{-i\theta} + x + e^{-i\theta} &= 0 \\
x &= -\left(e^{i\theta} + e^{-i\theta}\right) \\
&= -2\cos\theta \\
&= -2\cos 2j\pi/N \qquad (8.59)
\end{aligned}
$$

Since
$$
\begin{aligned}
x &= (\alpha - E)/\beta \\
E &= \alpha + 2\beta\cos 2j\pi/N \qquad (8.60)
\end{aligned}
$$

where
$$j = 0, \pm 1, \pm 2, \pm 3$$

The molecular orbital can be written as

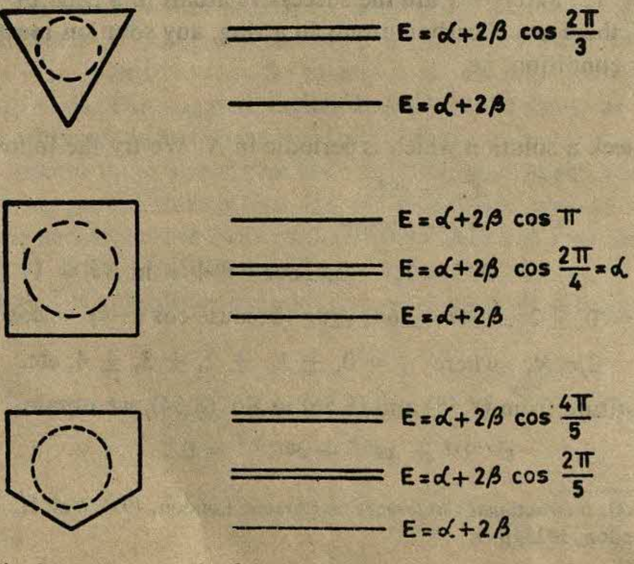
$$
\begin{aligned}
\psi &= \sum_r C_r\phi_r \\
&= \sum_r e^{ir\theta}\phi_r \\
&= \sum_r e\left(i\frac{2\pi j}{N}r\right)\phi_r
\end{aligned}
$$

Or the normalised wavefunction is given by

$$\psi = 1/\sqrt{N}.\sum_r e\left(i\frac{2\pi j}{N}r\right)\cdot\phi_r \qquad (8.61)$$

where j is called the ring quantum number, r is the running index over the atom of the ring and N is the total number of the atoms in the ring.

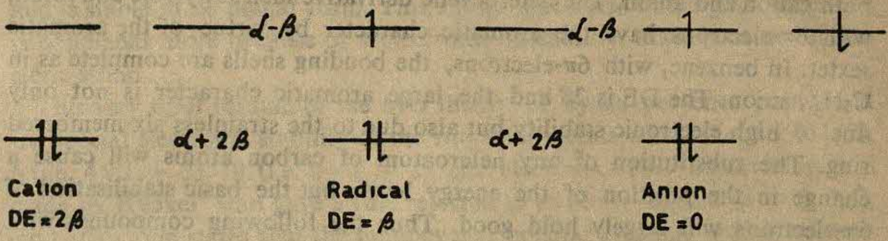
Since the total number of linearly independent molecular orbitals is equal to the number of atomic orbitals, i.e. N, when N is odd, the possible values of j are $0, \pm 1, \pm 2, \ldots \pm \frac{N-1}{2}$ and when N is even, the possible values of j are $0, \pm 1, \pm 2, \ldots \pm N/2$. This means that for an odd membered ring, except the lowest MO, all other orbitals occur in pairs (degenerate) while for an even membered ring, except the lowest and the highest MOs all the remaining orbitals occur in pairs (Fig. 8.7). Each set of energy levels may be thought of as a shell.



$E = \alpha + 2\beta\cos\frac{2\pi}{3}$
$E = \alpha + 2\beta$
$E = \alpha + 2\beta\cos\pi$
$E = \alpha + 2\beta\cos\frac{2\pi}{4} = \alpha$
$E = \alpha + 2\beta$
$E = \alpha + 2\beta\cos\frac{4\pi}{5}$
$E = \alpha + 2\beta\cos\frac{2\pi}{5}$
$E = \alpha + 2\beta$

Fig. 8.7 *Energy levels of three-, four- and five-membered rings*

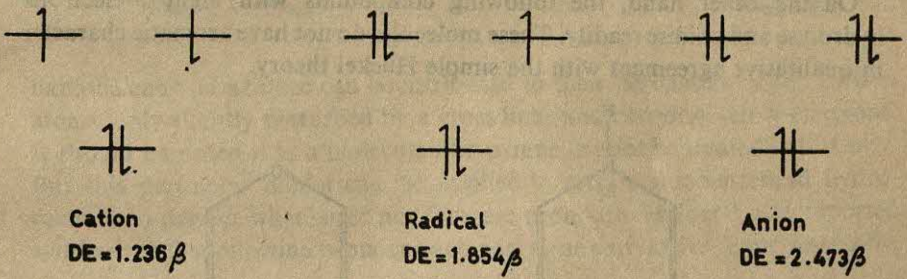
The cyclo-propenyl system can form cation, radical and anion with the following electron configurations:



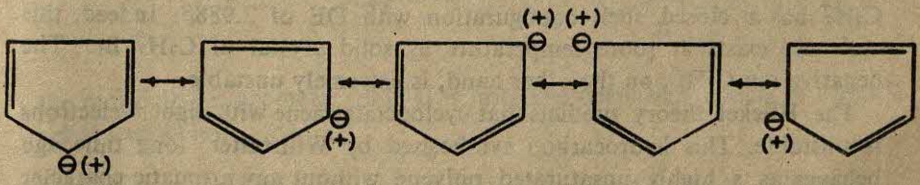
This shows that cation has the largest stability. Although the parent cation has not been isolated the triphenyl derivative[8] has been synthesised and is found to be stable.

The cyclobutadiene ring with four π-electrons has zero delocalisation energy (see answer to Problem 1). Several attempts to prepare cyclobutadiene have failed; however, some experiments have shown that it is capable of existence at least transiently.

The cyclopentadiene cation, radical and anion have the following electronic configurations:



This shows that, of these three species, $C_5H_5^-$ anion is most stable. The relatively high stability of this anion is reflected in the high acidity of cyclopentadiene and it reacts with potassium to form $K^+C_5H_5^-$. On the other hand, it is difficult to prepare the carbonium ion $C_5H_5^+$. Hence the MO theory succeeds in predicting the high stability of anion compared to that



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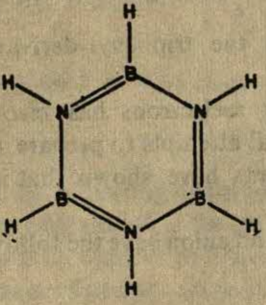
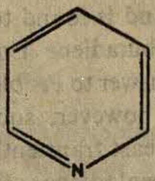
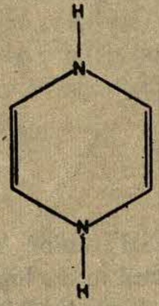
[8] R. Breslow and C. Yuan, *J. Am. Chem. Soc.* **80**, 5991, 1958.

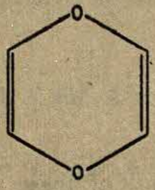
of cation, whereas the classical resonance theory predicts those two ions to be equally stable because of equal number of resonance structures in both cation and anion. The heterocyclic derivative such as pyrrole and furan, with 6π-electrons have the aromatic character by virtue of the aromatic sextet. In benzene, with 6π-electrons, the bonding shells are complete as in $C_5H_5^-$, anion. The DE is 2β and the large aromatic character is not only due to high electronic stability but also due to the strainless six-membered ring. The substitution of any heteroatom of carbon atoms will cause a change in the position of the energy levels but the basic stabilisation of 6π-electrons will largely hold good. Thus the following compounds with 6π-electrons are stable and aromatic.





On the other hand, the following compounds with eight π-electrons hydrolyse and oxidise readily. These molecules do not have aromatic character in qualitative agreement with the simple Hückel theory.





Tropylium radical with seven π-electrons has a delocalisation energy 2.543β. Even though this is quite high, the radical is unstable, oxidises easily and its ionisation potential is very low (6.60 eV). On the other hand the $C_7H_7^+$ has a closed shell configuration with DE of 2.988β: Indeed, this molecule exists at room temperature as solid crystal of $C_7H_7^+$ Br^-. The negative ion $C_7H_7^+$, on the other hand, is extremely unstable.

The Hückel theory predicts that cyclooctatetraene with eight π-electrons is unstable. This hydrocarbon synthesised by Willstatter[9] long time ago behaves as a highly unsaturated polyene without any aromatic character and has nonplanar tub-like structure. On the other hand, the dianion $C_8H_8^{=}$ with ten π-electrons forms a closed shell and has a DE of 3.657β. and is stable in its planar form. This shows that C_8H_8 with eight π-electrons is nonplanar more because of π-electronic instability than because of the steric strain.

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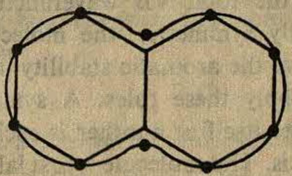
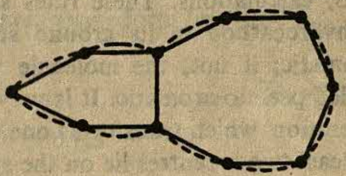
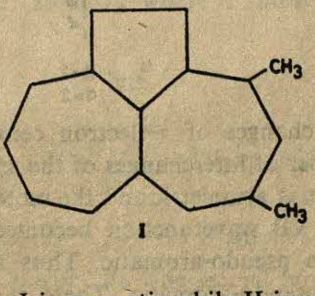
[9] R. Willstatter and E. Waser, Ber. **44**, 3423, 1911.

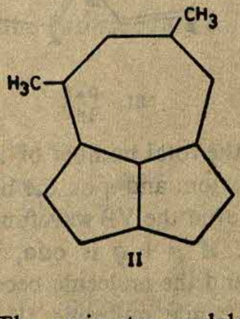
This very brief resume of the MO theory of cyclic polyenes points out the special electronic stability of the ring compounds with 2 (i.e. $4\times0+2$), 6 (i.e. $4\times1+2$), 10 (i.e. $4\times2+2$), etc. electrons. This observation was made by Hückel[7] who gave a rule referred to as $(4n+2)$ rule ($n=0, 1, 2,$ etc.). This rule states that the monocyclic coplanar systems, which contain $(4n+2)$ π-electrons will possess a large electronic stabilitv. The large stability is due to the closed shell configuration of electrons as in inert gas atoms. This rule appears to apply not only to monocyclic systems but also to the catacondensed hydrocarbons in which every unsaturated carbon atom is assumed to lie on the perimeter[10] of the molecule. Thus the aromaticity of naphthalene and azulene can be attributed to their perimeters of ten carbon atoms, only slightly perturbed by a cross link, and carrying ten π-electrons. It should be noted that a molecule like pyrene cannot be treated in this way. But this perimeter model can be applied to certain nonbenzenoid hydrocarbons to predict whether or not they are aromatic. Hafner[11] has reported synthesis of the following heptalene and pentalene derivatives. Experimentally, the molecule I is aromatic while II is not. The perimeter models of I and II are shown below.







I



II

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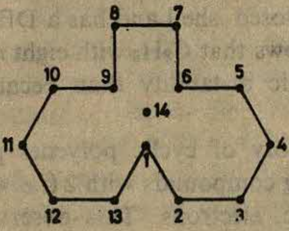
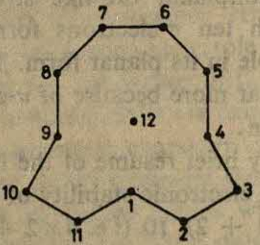
[10] M.J.S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345, 1952; M.J.S. Dewar and R. Pettit, *J. Chem. Soc.*, 1617, 1954.

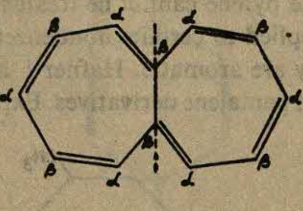
[11] K. Hafner J. Schneider, *Angew. Chem.*, **70**, 702, 1958; Ann., **624**, 37, 1959.



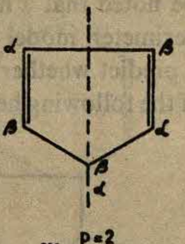


These perimeters are cyclic polyenes with 13 and 11 carbon atoms, each C-atom carrying one π-electron. Now we add one π-electron to each cyclic polyene. We then have cyclic systems with 14 and 12 electrons respectively. Therefore, the molecule I belongs to $(4n + 2)$ class ($n = 3$) and hence aromatic while the molecule II belongs to $4n$ class ($n = 3$) and hence non-aromatic.

Craig[12] has given a set of rules for aromaticity, based on valence bond (VB) calculations. These rules say that if the total VB wavefunction of a hydrocarbon in its ground state is totally symmetric, the molecule is aromatic; if not, the molecule will not have the aromatic stability and is called pseudo-aromatic. It is very easy to apply these rules. A symmetry operation which transforms one structure into itself or another is such that at least two π-centres lie on the symmetry axis. The molecule is first labelled with equal number of spin symbols α and β as far as possible. Alternatively, different symbols may be given to the ends of all the double bonds, in one Kekule structure, as shown below.



III $p = 5$ $q = 0$



IV $p = 2$ $q = 2$

Let p be the total number of interchanges of π-electron centres effected by the operation, and q be the number of interchanges of the spin symbols. If $p + q$ is even the VB wavefunction is symmetric and the molecule should be aromatic. If $p + q$ is odd, the VB wavefunction becomes nontotally symmetric and the molecule becomes pseudo-aromatic. Thus molecule IV is aromatic while molecule III is pseudo-aromatic. There is no obvious reason why electronic asymmetry should destroy the stability of a molecule, so that Craig's work does not entirely clear up the matter. However, this rule works with success and is used to predict whether or not a given hydrocarbon is aromatic.

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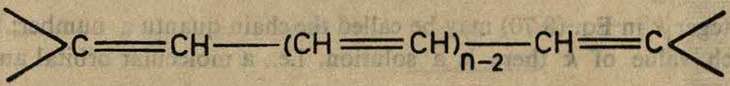
[12] D.P. Craig in *Theoretical Organic Chemistry. The Kekula Symposium,* Butterworths Scientific.

8.7 Huckel Treatment of the Linear Polyenes

Let us consider the polymethine dyes of the carotenoid type with $N = 2n$



number of conjugated carbon atoms. As in cyclic polyenes, one of the secular equations [see Eqs. (8.18) and (8.20)] is given by

$$C_{m-1} + xC_m + C_{m+1} = 0 \tag{8.62}$$

where $m - 1$, m and $m + 1$ are the successive atoms in a chain. We consider here a chain of carbon atoms with $m = 1$ and $m = N$ then

$$C_0 = 0 \quad \text{and} \quad C_{N+1} = 0 \tag{8.63}$$

These are the boundary conditions for linear polyene of finite length. We therefore look for a periodic solution guided by the fact that for an electron in a linear box, the wave functions are of sine and cosine form (see Sec 3.2). We assume

$$C_m = \exp(im\theta) \tag{8.64}$$

where θ is a constant. Following Eq. (8.62) one obtains

$$e^{i(m-1)\theta} + xe^{im\theta} + e^{i(m+1)\theta} = 0$$

$$e^{im\theta}[e^{-i\theta} + x + e^{i\theta}] = 0$$

or

$$x = -[e^{-i\theta} + e^{i\theta}] = -2\cos\theta \tag{8.65}$$

Since $\cos(-\theta) = \cos\theta$ it follows also that $C_m = e^{-im\theta}$ satisfies the Eq. (8.62) and that

$$C_m = A\exp(im\theta) + B\exp(-im\theta) \tag{8.66}$$

will be a general solution where A and B are the two arbitrary constants. Since $C_0 = 0$

$$A + B = 0 \tag{8.67}$$

and hence

$$\begin{aligned} C_m &= A[\exp(im\theta) - \exp(-im\theta)] \\ &= 2Ai\sin m\theta \\ &= D\sin m\theta \end{aligned} \tag{8.68}$$

where we write D for $2Ai$. The second boundary condition i.e., $C_{N+1} = 0$ gives

$$C_{N+1} = D\sin(N+1)\theta = 0$$

or

$$\begin{aligned} \sin(N+1)\theta &= 0 \\ (N+1)\theta &= k\pi \end{aligned} \tag{8.69}$$

where $k = 0, 1, 2, 3$, etc., and

$$\theta = \frac{k\pi}{N+1} \tag{8.70}$$

The integer k in Eq. (8.70) may be called the chain quantum number; thus for each value of k there is a solution, i.e., a molecular orbital and its energy.

Let us consider the energy levels. We substitute for θ, Eq. (8.70) in Eq. (8.65) and obtain

$$X = -2\cos\frac{k\pi}{N+1} \tag{8.71}$$

Since $x = \dfrac{\alpha - E}{\beta}$, we have the k^{th} energy level as

$$E^{(k)} = \alpha + 2\beta\cos\frac{k\pi}{N+1} \tag{8.72}$$

Finally, the coefficient of the m^{th} atomic orbital in the k^{th} molecular orbital is given by (use Eq. 8.68)

$$C_m^{(k)} = D_{(k)}\sin\left[\frac{mk\pi}{N+1}\right] \tag{8.73}$$

These are the required solutions for all linear polyene chains, no matter how many carbon atoms (N) there may be. It should be noted that $k = 0$ is not permissible because the wavefunction of polyene then becomes zero. Since π-electrons are present, wavefunction cannot vanish. So the permissible values of k in the above equations are 1, 2, 3, etc., or any positive integer. The constant $D_{(k)}$ in Eq. (8.73) can be chosen so as to normalise the MO and takes the value $D_{(k)} = \sqrt{2/(N+1)}$.

Since there are N distinct atoms in the linear polyenes there are N distinct solutions or energy levels according to Eq. (8.72). If we try

$$k = N+1,\quad N+2, \ldots$$

we simply find repetitions of the results for $k = 1, 2, \ldots$, etc. Thus, for a N-membered linear chain we find N energy levels. These levels are symmetrically disposed about $E = \alpha$ which is the energy of a π-electron in a carbon atom. The energy levels that have lower energies are called bonding MOs and those with higher energies are called antibonding MOs. When N is odd there is always a solution with $x = 0$ i.e., $E = \alpha$. This refers to the non-bonding MO. In Fig. 8.8 is shown the distribution of energy levels for a linear polyene. As N increases the density of the levels increases. When N is very large and $k = 1$ the energy of the lowest occupied MO is given by [from Eq. (8.72)]

$$E^{(1)} = \alpha + 2\beta \quad \text{since} \quad \cos\left(\frac{k\pi}{N+1}\right) \approx \cos 0 = 1$$

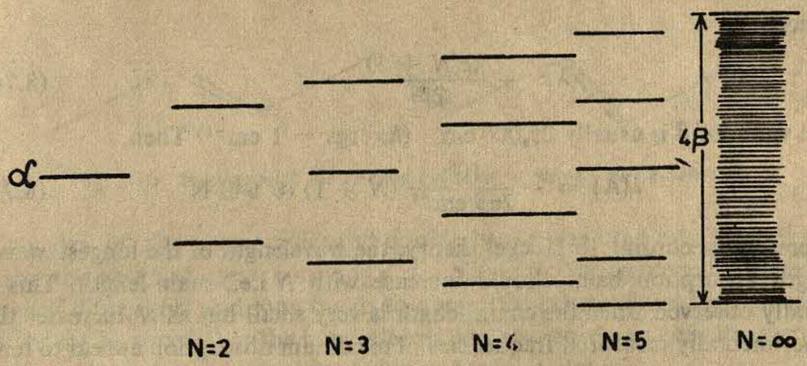


Fig. 8.8 *Distribution of energy levels for a linear polyene of N carbon atoms*

When both N and k are very large, the energy of the highest unoccupied MO is given as

$$E^{(k)} = \alpha - 2\beta; \qquad \text{since } \cos\left(\frac{k\pi}{N+1}\right) \approx \cos\pi = -1$$

Thus as the chain becomes infinitely large we obtain continuous band of levels within the width of 4β. This should make an infinitely long chain polyene a conductor of electricity like metals. But the experimental fact suggests that there is always a finite gap between the filled and the unfilled energy levels in a long chain polyene.

Various examples of polyene spectra can be found in the literature[13]. The longest wavelength band of a polyene can be correlated with the transition from the highest occupied MO i.e., $\psi^{(k)}$ $(k = n)$ to the lowest unoccupied MO i.e., $\psi^{(k)}$ $(k = n + 1)$. The energy difference is given by

$$\begin{aligned} \Delta E &= E_{n+1} - E_n \\ &= 2\beta\left[\cos\frac{(n+1)\pi}{N+1} - \cos\frac{n\pi}{N+1}\right] \\ &= -4\beta\sin\frac{\pi}{2(N+1)} \end{aligned} \tag{8.74}$$

The wavelength of the lowest energy band is then

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E} = -\frac{hc}{4\beta\sin[\pi/(2N+2)]} \tag{8.75}$$

For large N

$$\sin\left[\frac{\pi}{(2N+2)}\right]$$

tends to

$$\left[\frac{\pi}{(2N+2)}\right]$$

---

[13] M. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.

hence

$$\lambda \simeq -\frac{hc(N+1)}{2\beta\pi} \qquad (8.76)$$

The value of β is usually 25,000 cm^{-1} (hc ergs = 1 cm^{-1}) Then,

$$\lambda(\text{Å}) = -\frac{10^8}{2\pi\beta\ \text{cm}^{-1}}(N+1) \approx 640\ \text{N} \qquad (8.77)$$

Therefore, according to Hückel theory, the wavelength of the longest wavelength absorption band should increase with N i.e., chain length. This is usually observed when the chain length is very small but as N increases the experimentally measured frequencies of maximum absorption appear to tend toward a finite limit ($\tilde{\nu}$ = 18,000 cm^{-1}). In Fig. 8.9 the observed wavenumbers ($\tilde{\nu} = \nu/c$) of maximum absorption are plotted against n for linear polyenes. This observation suggests that there is a finite energy gap between the filled and unfilled electronic levels as the chain length increases indefinitely.

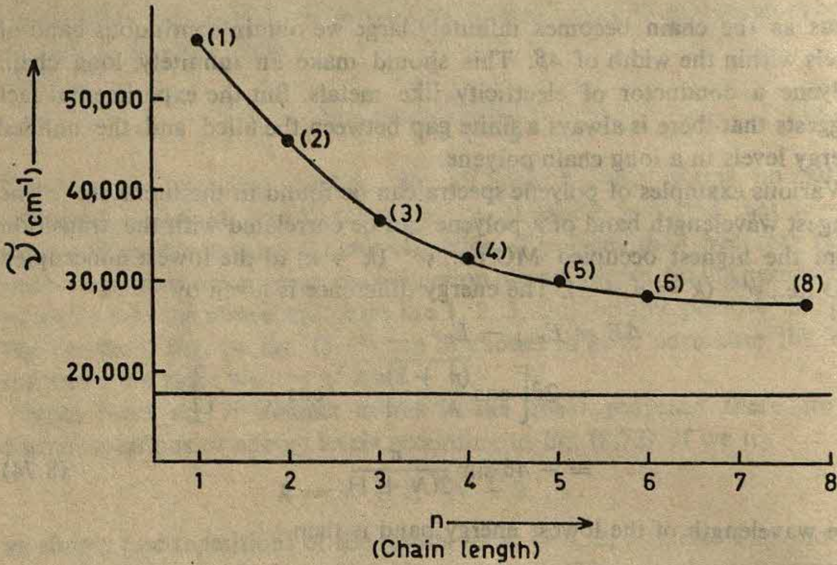


Fig. 8.9 *Wavenumbers of maximum absorption plotted against chain length*

A satisfactory explanation of this phenomenon was put forward by Kuhn[14] who said that in large polyenes the π-delocalisation is not so extensive and that the π-electrons are somewhat clustered in localised regions. He put forward that alternate bonds in polyene are actually double (short) and single (long). In other words, the real physical situation would be best described by the classical picture of alternate double and single bonds as in Fig. 8.10.

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[14] H. Kuhn, *J. Chem. Phys.*, 16, 840, 1948.

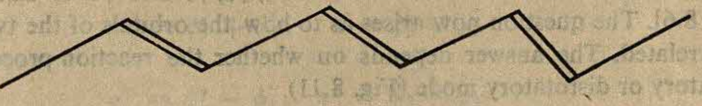


Fig. 8.10 *Polyene with the alternate double bonds and single bonds*

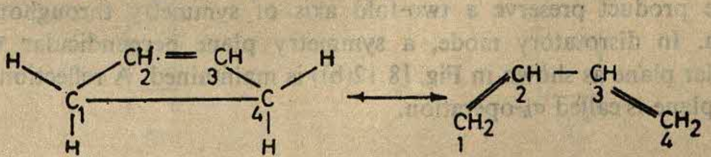
The idea of alternate single and double bonds was used by Dewar[15] to explain the observed spectra in long chain polyenes. He employed different values of β for short and long bonds to obtain the experimental frequencies.

It should be noted that the bond alternation also exists in infinite cyclic polyenes where the unsymmetric structure becomes stable.[16]

8.8 Theory of Electrocyclic Reactions: Woodward-Hoffmann Rule

Hückel molecular orbital theory, inspite of its empiricism and approximations, is capable of providing significant interpretations of chemical reactivity in organic molecules. A detailed discussion on wave-mechanical theory of chemical reaction is beyond the scope of this book. However, we shall describe here the great contribution of Woodward and Hoffmann[17] who have developed, using correlation diagrams, a general rule which enables one to predict the possible reaction paths in electrocyclic reactions. The basic principle employed by them was that a chemical reaction proceeds with the conservation of orbital symmetry.

Electrocyclic reaction is defined as the formation of a single bond between the termini of linear conjugated system and the converse process. An interesting example is the inter-conversion of cyclobutene to butadiene.



In this process the single 1-4 σ-bond in cyclobutene is broken. This bond is formed from the overlap of two sp^3-hybrids. For simplicity, only the p-character of the orbital will be emphasised. We shall deal with only those relevant bonds which participate in this reaction. The C–H bonds which do not directly take part in this reaction will not affect its course materially. In the conversion of cyclobutene to butadiene, σ and σ^* orbitals (i.e. bonding and antibonding) of 1–4 σ-bond and π and π^* orbitals (i.e. bonding and antibonding) of 2–3 π-bond in cyclobutene pass adiabatically to four π-molecular orbitals of butadiene [i.e. ψ_1, ψ_2, ψ_3 and ψ_4 of Eq. (8.53) or Fig. 8.6]. The question now arises as to how the orbitals of the two sets are correlated. The answer depends on whether the reaction proceeds in conrotatory or disrotatory mode (Fig. 8.11).

---

[15] M.J.S. Dewar, *J. Chem. Soc.*, 3544, 1952.

[16] L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, Benjamin, New York, 1966, Chap. 8.

[17] R.B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395; 2511, 1965.

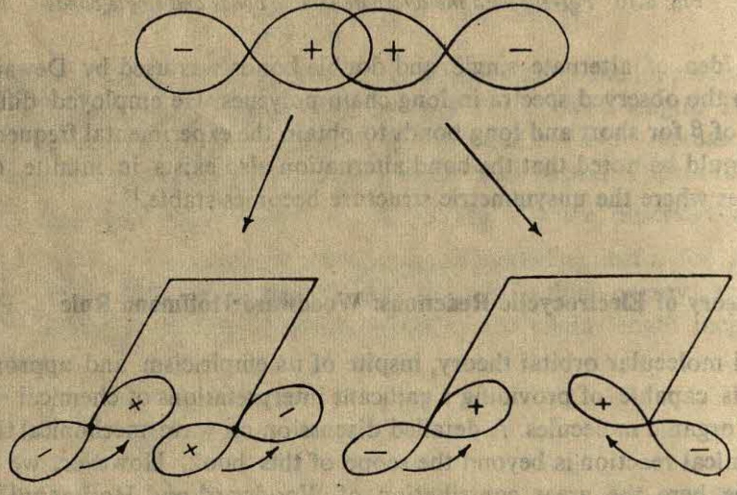


Fig. 8.11 *Rearrangement of cyclobutene to butadiene*

Either mechanism assumes that the breaking of σ-bond and its rearrangement to a π-bond is concerted. Now consider an axis passing through the centres of 2–3 and 1–4 bonds in cyclobutene [Fig. 8.12(a)]. A rotation by 180° about this axis is called a c_2-operation and the axis a two-fold axis. Clearly, when the reaction occurs in conrotatory fashion, both the reactant and the product preserve a two-fold axis of symmetry throughout the reaction. In disrotatory mode, a symmetry plane perpendicular to the molecular plane as shown in Fig. [8.12(b)] is maintained. A reflection from such a plane is called σ_h-operation.

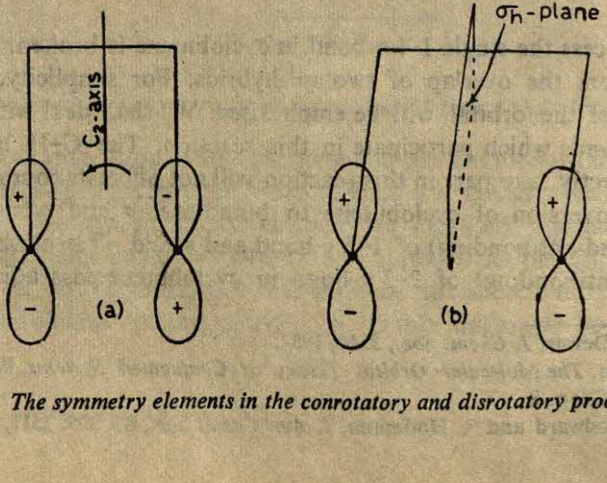


Fig. 8.12 *The symmetry elements in the conrotatory and disrotatory processes*

The σ, $\sigma*$ and π, $\pi*$ orbitals of cyclobutene are given by

$$\begin{aligned} \sigma &= \phi_1' + \phi_4' \qquad \pi = \phi_2 + \phi_3 \\ \sigma^* &= \phi_1' - \phi_4' \qquad \pi^* = \phi_2 - \phi_3 \end{aligned} \tag{8.78}$$

where ϕ_1', ϕ_4' are the $p\sigma$-orbitals on atoms 1 and 4 along the direction of the 1–4 bond, ϕ_2, ϕ_3 are the p_π-orbitals on atoms 2 and 3, the normalisation factors being omitted for convenience. A schematic diagram of these orbitals is shown in Fig. 8.13. These orbitals may be classified according as they are symmetric or antisymmetric with respect to two-fold axis.

$$\begin{aligned} c_2\sigma &= c_2(\phi_1' + \phi_4') = \phi_4' + \phi_1' = \sigma : S \\ c_2\sigma^* &= c_2(\phi_1' - \phi_4') = \phi_4' - \phi_1' = -\sigma^* : A \\ c_2\pi &= c_2(\phi_2 + \phi_3) = -\phi_3 - \phi_2 = -(\phi_3 + \phi_2) = -\pi : A \\ c_2\pi^* &= c_2(\phi_2 - \phi_3) = -\phi_3 + \phi_2 = \pi^* : S \end{aligned}$$

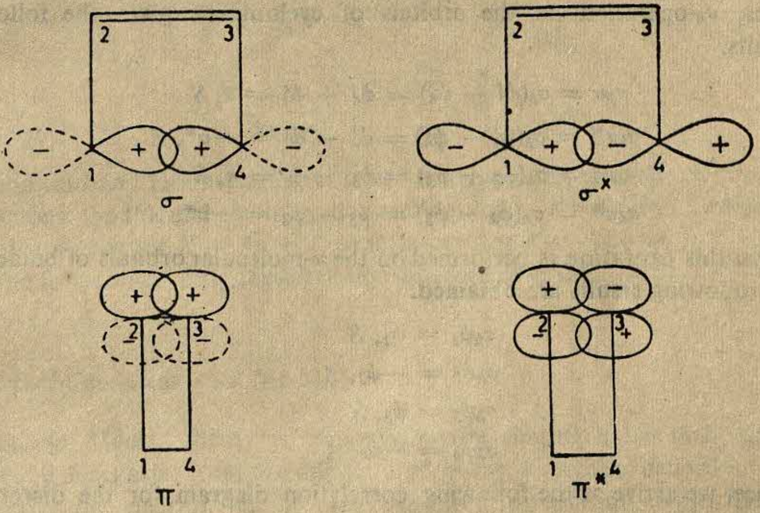


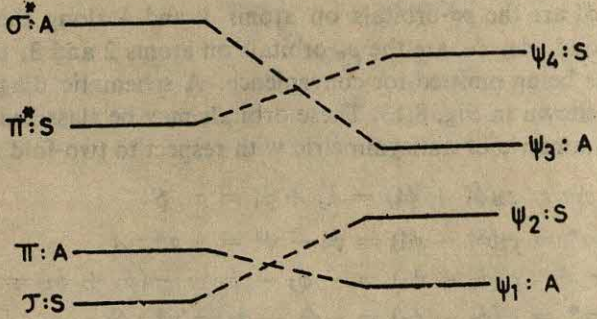
Fig. 8.13 *The schematic diagram of* σ, σ^* *and* π, π^* *orbitals in cyclobutene*

Thus, σ and π^* orbitals are symmetric (S) and σ^*, π orbitals, antisymmetric (A) with respect to c_2-operation. When c_2-operation is performed on four π-molecular orbitals of butadiene the following results are obtained.

$$\begin{aligned} c_2\psi_1 &\doteq c_2[0.375(\phi_1 + \phi_4) + 0.607(\phi_2 + \phi_3)] \\ &= 0.375(-\phi_4 - \phi_1) + 0.607(-\phi_3 - \phi_2) = -\psi_1 : A \\ c_2\psi_2 &= c_2[0.607(\phi_1 - \phi_4) + 0.375(\phi_2 - \phi_3)] \\ &= 0.607(-\phi_4 + \phi_1) + 0.375(-\phi_3 + \phi_2) = \psi_2 : S \\ c_2\psi_3 &= c_2[0.607(\phi_1 + \phi_4) - 0.375(\phi_2 + \phi_3)] \\ &= 0.607(-\phi_4 - \phi_1) - 0.375(-\phi_3 - \phi_2) = -\psi_3 : A \end{aligned}$$

$$
\begin{aligned}
c_2\psi_4 &= c_2[0.375(\phi_1 - \phi_4) - 0.607(\phi_2 - \phi_3)] \\
&= 0.375(-\phi_4 + \phi_1) - 0.607(-\phi_3 + \phi_2) = \psi_4 : S
\end{aligned}
$$

We are now in a position to draw the following correlation diagram for the conrotatory conversion process.



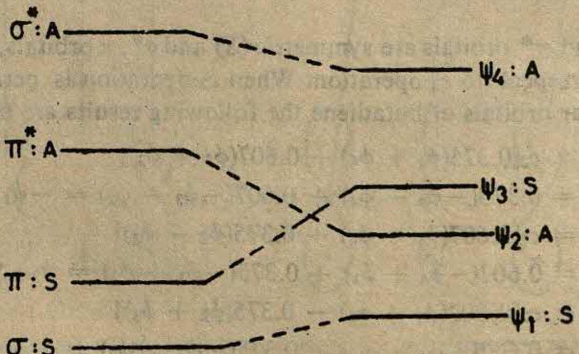
For the disrotatory conversion process the correlations are different. Thus, σ_h-operation on the orbitals of cyclobutene gives the following results.

$$
\begin{aligned}
\sigma_h\sigma &= \sigma_h(\phi_1' + \phi_4') = \phi_4' + \phi_1' = \sigma, S \\
\sigma_h\sigma^* &= \sigma_h(\phi_1' - \phi_4') = \phi_4' - \phi_1' = -\sigma^*, A \\
\sigma_h\pi &= \sigma_h(\phi_2 + \phi_3) = \phi_3 + \phi_2 = \pi, S \\
\sigma_h\pi^* &= \sigma_h(\phi_2 - \phi_3) = \phi_3 - \phi_2 = -\pi^*, A
\end{aligned}
$$

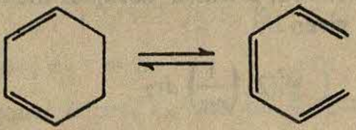
When this operation is performed on the π-molecular orbitals of butadiene, the following results are obtained.

$$
\begin{aligned}
\sigma_h\psi_1 &= \psi_1, S \\
\sigma_h\psi_2 &= -\psi_2, A \\
\sigma_h\psi_3 &= \psi_3, S \\
\sigma_h\psi_4 &= -\psi_4, A
\end{aligned}
$$

Hence, we arrive at the following correlation diagram for the disrotatory process.



Having correlated the orbitals of cyclobutene with those of butadiene via the conrotatory and disrotatory modes we can now correlate the electronic configurations of the two molecules. Clearly, the lowest energy configuration $\sigma^2\pi^2$ of cyclobutene correlates with the ground state $\psi_1^2\psi_2^2$ of butadiene for conrotatory mode and with higher energy or less stable state $\psi_1^2\psi_3^2$ of butadiene for disrotatory mode. It is, therefore, immediately obvious that conrotatory route is energetically more favourable than disrotatory one for the thermal electrocyclic interconversion between cyclobutene and butadiene. On the other hand, the next excited configuration $\sigma^2\pi\pi^*$ of cyclobutene correlates with the configuration $\psi_1^2\psi_2^1\psi_4^1$ for conrotatory route and the more stable configuration $\psi_1^2\psi_2^1\psi_3^1$ of butadiene for disrotatory route. If electronic excitation of the π-bond were to initiate the reaction, disrotatory mode would be energetically most favourable. Therefore, the reaction path depends upon the way in which the reaction is carried out. The very same type of arguments using the Hückel molecular orbitals for the π-electrons show that photochemical and thermal reactions follow opposite routes for the interconversion of cyclohexa 1-3 diene to hexa 1-3-5 triene. Thus,



Woodward and Hoffmann have arrived at the general rules for electrocyclic reactions: the thermal electrocyclic reactions of a $K\pi$-electron system will be disrotatory for $K = 4n + 2$, conrotatory for $K = 4n (n = 0, 1, 2, \ldots)$; in the first excited state these relationships are reversed.

8.9 Self-Consistent Field Method

Although Hückel theory is computationally simple, it has many defects. These defects arise from the difficulty of giving a precise definition of an effective one-electron hamiltonian. An electron repulsion energy term like e^2/r_{ij} depends on the coordinates of both electrons and cannot be replaced by any one-electron potential energy term. This failure to consider electron repulsion adequately leads to a poor approximation of excited state phenomena and unmeaningful charge distribution of a molecule in its ground state. However, in closely related series of molecules, the neglect of electron repulsion may be minimal in its influence, hence sometimes satisfactory correlations between some Hückel calculated and observed properties may be obtained. The general situation is, therefore, not encouraging.

The self-consistent field (SCF) formulation of the molecular orbital theory based on the many-electron hamiltonian has been developed by Roothan.[18] These are simplified by systematic approximation of the integrals and reduced to expressions involving empirical parameters analogous to those of Hückel theory, together with electron interaction terms, by Pariser and Parr,[19] and Pople.[20]

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[18] C.C.J. Roothan, *Rev. Mod. Phys.*, **23**, 69, 1951.

For a π-electron system, the hamiltonian operator is expressed in a.u. as

$$\hat{H} = \sum_{i}^{\text{all electrons}} \hat{H}_i\,(\text{core}) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \tag{8.79}$$

The first term in Eq. (8.79) determines the attraction energy of the core for the π-electron. This is a one-electron operator as it depends on the coordinates of one electron only and is given by

$$\hat{H}_i\,(\text{core}) = -\tfrac{1}{2}\nabla_i^2 - \sum_{a}^{\text{all nuclei}} \frac{Z_a}{r_{ia}} \tag{8.80}$$

where Z_a is the nuclear charge on nucleus, a, r_{ia}, the distance of an electron i from nucleus, a. Each $1/r_{ij}$ term in Eq. (8.79) involves the coordinates of both electrons simultaneously and cannot be evaluated exactly. This term can be approximated by considering an electron, say 1 subjected to the average field of an electron, 2 which occupies the molecular orbital, say ψ_i. This average field is given by

$$\int \psi_i^2(2) \left(\frac{1}{r_{12}}\right) d\tau_2$$

Since electrons can exchange between the molecular orbitals, this can be considered by including the term

$$-\int \psi_i(2)\psi_j(2) \left(\frac{1}{r_{12}}\right) d\tau_2$$

These two terms ought to be summed over all the occupied molecular orbitals. Therefore the eigenvalue equation to be solved for an electron 1 in molecular orbital say $\psi_j(1)$ is given by

$$[\sum_{i}^{\text{all electrons}} \hat{H}_i(\text{core}) + \sum^{\text{Occ. MOs}} (2J_i - K_i)]\psi_j(1) = \epsilon_j\psi_j(1) \tag{8.81}$$

where
$$\hat{J}_i\psi_j(1) = \left\{\int \psi_i^2(2) \left(\frac{1}{r_{12}}\right) d\tau_2\right\}\psi_j(1) \tag{8.82}$$

$$\hat{K}_i\psi_j(1) = \left\{\int \psi_i(2)\psi_j(2) \left(\frac{1}{r_{12}}\right) d\tau_2\right\}\psi_i(1) \tag{8.83}$$

The operators $\hat{J}$ and $\hat{K}$ are called Coulomb and exchange operators. Since each molecular orbital is occupied by two electrons, Coulomb term will be double; however, the exchange term will remain a single term as this will become zero unless the molecular orbitals ψ_i and ψ_j refer to the same spin functions. The operator on the left hand side of Eq. (8.81) is called an effective Fock-operator ($\hat{F}$) and the eigenvalue equation is simply written as

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[19] R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 466, 767, 1953.

[20] J.A. Pople, *Trans. Faraday Soc.*, **49**, 1375, 1953.

$$\hat{F}\psi_i = \epsilon_i\psi_i \tag{8.84}$$

As in simple Hückel theory, the molecular orbitals are built up in the LCAO form as

$$\psi_i = \sum^{\text{all AOs}} C_{ij}\phi_j \tag{8.85}$$

Application of the variation method leads to a set of secular equations which in determinant form are given by

$$\begin{vmatrix} \alpha_{11} - \epsilon & \beta_{12} - S_{12}\epsilon & \beta_{13} - S_{13}\epsilon \ldots \\ \beta_{12} - S_{12}\epsilon & \alpha_{22} - \epsilon & \beta_{23} - S_{23}\epsilon \ldots \\ \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{8.86}$$

where

$$\begin{aligned} \langle \phi_i \mid F \mid \phi_i \rangle &= F_{ii} = \alpha_i \\ \langle \phi_i \mid F \mid \phi_j \rangle &= F_{ij} = \beta_{ij} \\ \langle \phi_i \mid \phi_j \rangle &= S_{ij} \end{aligned} \tag{8.87}$$

Evaluation of the diagonal terms, α_i, and off diagonal terms, β_{ij}, gives (see Appendix 8)

$$\alpha_i = \alpha_i\,(\text{core}) + \tfrac{1}{2}q_i \langle \phi_i\phi_i \mid \phi_i\phi_i \rangle + \sum_{j\neq i} q_j \langle \phi_i\phi_i \mid \phi_j\phi_j \rangle \tag{8.88}$$

$$\beta_{ij} = \beta_{ij}\,(\text{core}) - \frac{1}{2}\,p_{ij} \langle \phi_i\phi_i \mid \phi_j\phi_j \rangle \tag{8.89}$$

where q_i is the total π-electron density on atom i, p_{ij} is the mobile bond order if i and j are the neighbouring atoms linked directly. αi (core) and β_{ij} (core) are defined as

$$\alpha_i\,(\text{core}) = \langle \phi_j \mid \sum_i^{\text{all electrons}} H_i\,(\text{core}) \mid \phi_j \rangle, \quad i = j \tag{8.90}$$

$$\beta_{ij}\,(\text{core}) = \langle \phi_i \mid \sum_i^{\text{all electrons}} H_i\,(\text{core}) \mid \phi_j \rangle \; i \neq j,$$

atom i being linked to atom j (8.91)

$$= 0, \qquad \text{otherwise} \tag{8.92}$$

The integral $\langle \phi_i\phi_i \mid \phi_i\phi_i \rangle$ in Eq. (8.88) describes the electron repulsion between two electrons in the field of the same core, and, $\langle \phi_i\phi_i \mid \phi_j\phi_j \rangle$ in Eq. (8.89), between two electrons on the neighbouring cores ϕ_i and ϕ_j. With these equations for αs and βs, the secular determinant is solved for coefficients, and hence the charges and bond orders. This set of q and p values is used to compute an improved set of α and β values and the process is iterated until the convergence is achieved.

8.10 Valence State Ionisation Potentials

Consider an atom in which electrons are placed in suitably hybridised orbitals. The atom is then said to be promoted to a valence state. In other words, the valence state of an atom is a state which is prepared through electronic rearrangement prior to the bond formation. In the localised-bond model, a carbon atom in a conjugated system is supposed to be in an sp^2-hybridised state. Such carbon atom is represented by the configuration:

$$1s^2(tr_1)^1(tr_2)^1(tr_3)^1(2p_z)^1 \tag{8.93}$$

where tr_1, tr_2, tr_3 are trigonal hybrids formed from $2s$, $2p_x$, $2p_y$-orbitals. One may assume without any serious error that the configuration of a carbon atom given by (8.93) is equivalent to that given by

$$1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1 \tag{8.94}$$

because three electrons occupying the hybrid orbitals that have $1/3s$ and $2/3$ p-characters should be equivalent to one electron occupying the s-atomic orbital and two occupying p-atomic orbitals. Thus, the valence state ionisation potential of $2p_z$ orbital in carbon is given by the difference in energy between neutral carbon in the configuration (8.94) and the ion C^+ in the configuration:

$$1s^2(2s)^1(2p_x)^1(2p_y)^1 \tag{8.95}$$

Similarly, the valence state ionisation potential of $2s$-orbital in carbon is given by the energy difference between the configuration (8.94) and the following configuration of C^+:

$$(1s)^2(2p_x)^1(2p_y)^1(2p_z)^1 \tag{8.96}$$

The most commonly used values of the valence state ionisation potentials are, -13.6 eV for hydrogen $1s$, -21.4 eV for carbon $2s$, -11.4 eV for carbon $2p$, -26.0 eV for nitrogen $2s$, -13.4 eV for nitrogen $2p$, -32.0 to -35.3 eV for oxygen $3s$, and -14.8 to -17.8 eV for oxygen $2p$.

8.11 The Pariser-Parr-Pople Approximation (PPP Approximation)

The semiempirical methods proposed by Pariser, Parr and Pople[19,20] (1953) to evaluate the parameters α_i (core), β_{ij} (core), the one-center and two-center electron repulsion integrals of Eqs. (8.88) and (8.89) are considered in this section. Consider the integral α_i (core). This is the energy required to remove a π-electron from the $2p_\pi$ atomic orbital of a carbon atom which is linked to three other atoms by bonds. Consider now the two ions C^+ and C^- formed by adding one electron to or removing one electron from this $2p_\pi$ orbital. The energy required to remove an electron from C to form C^+ is the corresponding valence state ionisation potential I_c. Then, by definition, one may write

$$\alpha_i\,(\text{core}) = -I_c \tag{8.97}$$

The energy liberated when an electron combines with $C^{\cdot}$ to form C^- is the corresponding valence state electron affinity, A_c. Consider the process

$$2C^{\cdot} \rightarrow C^+ + C^-: \tag{8.98}$$

The total energy change in this process should equal $I_c - A_c$. But there should be an additional energy arising from the mutual repulsion of two π-electrons in C^-. This is essentially the definition of the one-center integral, $\langle \phi_i\phi_i \mid \phi_i\phi_i \rangle$ for the i^{th} carbon atom. While the total energy of two π-electrons on two carbon atoms is $-2I_c$, the total energy of two π-electrons in C^- is $2I_c + \langle \phi_c\phi_c \mid \phi_c\phi_c \rangle$ where ϕ_c is a $2p_\pi$-orbital on a carbon atom. The change in energy involved in the process (8.98) is given by

$$[2I_c + \langle \phi_c\phi_c \mid \phi_c\phi_c \rangle] - 2I_c$$

$$= I_c - A_c$$

or

$$\langle \phi_c\phi_c \mid \phi_c\phi_c \rangle = I_c - A_c \tag{8.99}$$

Similar arguments can be put forward for other atoms and the one-center electron repulsion integrals are estimated in this way. For carbon, Pariser[21] obtained the value of 10.53 eV.

In the work of Pariser and Parr[19] the resonance integral β_{ij} (core) of Eq. (8.91) was taken to be zero for all orbitals except those on the nearest neighbouring atoms. They obtained the value of β_{ij} for C–C bond by fitting the observed spectroscopic data to the calculated differences in energy between the ground and excited states. Pariser and Parr estimated β_{ij} for C–C bond in benzene at -2.39 eV.

The values of two-center integrals, i.e., $\langle \phi_i\phi_i \mid \phi_j\phi_j \rangle$ depend on the internuclear separation R_{ij}. Let us use the symbol γ_{ij} for this two-center integral. The semiempirical method must obey the following boundary conditions. i.e.,

$$\left.\begin{aligned} &\gamma_{ij} = \gamma_{ii} \text{ (one center integral)} \\ &R_{ij} \rightarrow 0 \\ &\gamma_{ij} = e^2/R_{ij} \\ &R_{ij} \rightarrow \infty \end{aligned}\right\} \tag{8.100}$$

This approach is known as the Pariser-Parr-Pople (PPP) approximation. Pariser and Parr[19] however developed a method of determining the two-center electron repulsion integrals suited for π-electron calculations. This method is called the uniformly charged-sphere approximation. They suggested that the charge cloud on each $2p_\pi$-orbital could be replaced by two spheres each having charge of $-e/2$ uniformly distributed and the radius, d and touching at the corresponding nucleus, as shown in Fig. 8.14. The repulsion between these clouds can now be calculated according to Coulomb's law.

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[21] R. Pariser, *J. Chem. Phys.*, **21**, 568, (1953).

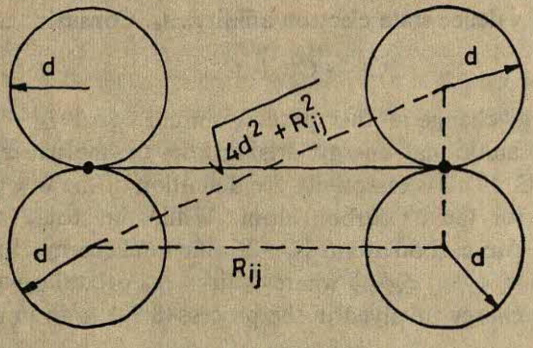

Fig. 8.14 *The uniformly charged sphere approximation for electron repulsion integrals*

In the case of two identical carbon atoms $d_i = d_j = d$, we have,

$$\langle \phi_i\phi_i \mid \phi_j\phi_j \rangle = 2\left[\frac{(-e/2)(-e/2)}{R_{ij}} + \frac{(-e/2)(-e/2)}{\sqrt{R_{ij}^2 + 4d^2}}\right]$$

$$= \frac{e^2}{2R_{ij}}\left[1 + \left(1 + \frac{4d^2}{R_{ij}^2}\right)^{-1/2}\right] \tag{8.101}$$

where the radius '*d*' is given by

$$d(\text{Å}) = \frac{2.298}{\rho} \tag{8.102}$$

and ρ is the orbital exponent of the $2p_\pi$ atomic orbital. For carbon, $\rho = 1.59$, Pariser and Parr found that Eq. (8.101) is valid for $R > 2.8$ Å. For $R < 2.8$ Å an exptrapolation to the one-center limit is made through the expression proposed by Parr[22]

$$\langle \phi_i\phi_i \mid \phi_j\phi_j \rangle = 1/2[\langle \phi_i\phi_i \mid \phi_i\phi_i \rangle + \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle] - aR - bR^2 \tag{8.103}$$

where a and b are determined by parabolic fitting to the values for $R = 2.8$ Å and $R = 3.7$ Å calculated using Eq. (8.101). For example, the two-center integral between the two $2p_\pi$-orbitals of carbon is given by Eq. (8.104) for $R < 2.8$ Å,

$$\langle \phi_i\phi_i \mid \phi_j\phi_j \rangle = 0.2157R^2 - 2.625R + 10.53 \tag{8.104}$$

where R is expressed in Å and the integral obtained in eV. Table 8.1 shows the values of one-center and two-center integrals between the two $2p_\pi$-orbitals of carbon for some distances.

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[22] R.G. Parr, *J. Chem. Phys.*, 20, 239, 1952.

Table 8.1 INTEGRALS OVER $2p_\pi$-ATOMIC ORBITALS OF CARBON

Integral	R(Å)	Values (eV)
$\langle \phi_1\phi_1 \mid \phi_1\phi_1 \rangle$	0.0	10.53
$\langle \phi_1\phi_1 \mid \phi_2\phi_2 \rangle$	1.35	7.38
	1.40	7.30
	1.46	7.16
	2.40	5.46
	2.78	4.90
	2.97	4.65

APPENDIX 8

In this appendix we shall derive Eqs. (8.88) and (8.89) from the definition of Fock Operator $\hat{F}$. The Operator $\hat{F}$ is given by

$$\hat{F} = \sum_i^{\text{all electrons}} H_i \quad (\text{core}) + \sum_i^{\text{Occ. MOs}} \quad (2J_i - K_i)$$

We shall neglect the differential atomic-orbital overlap, i.e.,

$$\phi_i\phi_j \approx 0$$

We shall first consider α_j:

$$\begin{aligned}\alpha_j &= \langle \phi_j(1) \mid \hat{F} \mid \phi_j(1) \rangle \\ &= \langle \phi_j(1) \mid \sum_i^{\text{all electrons}} H_i\,(\text{core}) \mid \phi_j(1) \rangle + \langle \phi_j(1) \mid \\ &\quad \sum_i^{\text{Occ.MOs}} (2J_i - K_i) \mid \phi_j(1) \rangle \\ &= \alpha_j\,(\text{core}) + \langle \phi_j(1) \mid \sum_i^{\text{Occ.MOs}} 2J_i \mid \phi_j(1) \rangle \\ &\quad - \langle \phi_j(1) \mid \sum_i^{\text{Occ.MOs}} K_i \mid \phi_j(1) \rangle \end{aligned} \tag{A8.1}$$

Now, we shall evaluate the integrals over $\hat{J}$ and $\hat{K}$ separately.

$$\langle \phi_j(1) \mid \sum_i^{\text{Occ.MOs}} 2J_i \mid \phi_j(1) \rangle = 2 \langle \phi_j(1) \mid \sum_i^{\text{Occ.MOs}} \int \psi_i^2(2)/r_{12}\, dv \mid \phi_j(1) \rangle$$

For the definition of $\hat{J}$ see Eq. (8.82). Using the LCAO form of ψ_i [Eq. (8.85)] and neglecting the differential AO-overlap one obtains

$$\begin{aligned}\langle \phi_j(1) \mid \sum_i^{\text{Occ.MOs}} 2J_i \mid \phi_j(1) \rangle &= 2 \sum_i^{\text{Occ.MOs}} C_{ij}^2 \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle \\ &\quad + 2 \sum_i^{\text{Occ.MOs}} \sum_{k \neq j}^{\text{AOs}} C_{ik}^2 \langle \phi_k\phi_k \mid \phi_j\phi_j \rangle\end{aligned}$$

Since $$q_j = 2 \sum_{i}^{\text{Occ.MOs}} C_{ij}^2 \quad \text{[see Eq. (8.26)]}$$

where each molecular orbital is doubly occupied, we have

$$\langle \phi_j(1) \mid \sum_{i}^{\text{Occ.MOs}} 2J_i \mid \phi_j(1) \rangle = q_j \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle + \sum_{k \neq j}^{\text{AOs}} q_k \langle \phi_k\phi_k \mid \phi_j\phi_j \rangle \qquad \text{(A8.2)}$$

Consider the integral over $\hat{K}$. From the definition of $\hat{K}$ [Eq. (8.83)] one obtains

$$\langle \phi_j(1) \mid \sum_{i}^{\text{Occ.MOs}} K_i \mid \phi_j(1) \rangle$$

$$= \langle \phi_j(1) \mid \sum_{i}^{\text{Occ.MOs}} \int \psi_i(2)\phi_j(2)/r_{12}\, dv \mid \psi_i(1) \rangle$$

$$= \sum_{i}^{\text{Occ.MOs}} . \, C_{ij}^2 \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle + \sum_{i}^{\text{Occ.MOs}} \sum_{k \neq j}^{\text{AOs}} C_{ik}^2 \langle \phi_k\phi_j \mid \phi_k\phi_j \rangle \qquad \text{(A8.3)}$$

Since the differential overlap is neglected, the second term in Eq. (A8.3) is zero. We have then

$$\langle \phi_j(1) \mid \sum_{i}^{\text{Occ.MOs}} K_i \mid \phi_j(1) \rangle = \sum_{i}^{\text{Occ.MOs}} C_{ij}^2 \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle$$

$$= (1/2) q_j \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle \qquad \text{(A8.4)}$$

The combination of Eqs. (A8.1), (A8.2) and (A8.4) gives

$$\alpha_j = \alpha_j\,(\text{core}) + 1/2 q_j \langle \phi_j\phi_j \mid \phi_j\phi_j \rangle + \sum_{k \neq j}^{\text{AOs}} q_k \langle \phi_k\phi_k \mid \phi_j\phi_j \rangle$$

The derivation of Eq. (8.89) proceeds as follow:

$$\beta_{ij} = \langle \phi_i(1) \mid \hat{F} \mid \phi_j(1) \rangle = \langle \phi_i(1) \mid \sum_{i}^{\text{all electrons}} H_i\,(\text{core}) \mid \phi_j(1) \rangle$$

$$+ \langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} (2\hat{J}_i - \hat{K}_i) \mid \phi_j(1) \rangle$$

$$= \beta_{ij}\,(\text{core}) + \langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} 2\hat{J}_i \mid \phi_j(1) \rangle$$

$$- \langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} \hat{K}_i \mid \phi_j(1) \rangle \qquad \text{(A8.5)}$$

In view of the zero-differential atomic orbital overlap approximation the second term in (A8.5) is zero. Consider the integral over $\hat{K}$.

$$\langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} \hat{K}_i \mid \phi_j(1) \rangle$$

$$= \langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} \int \psi_i(2)\phi_j(2)/r_{12}\, dv \mid \psi_i(1) \rangle$$

Using the LCAO form of ψ_i and neglecting the differential atomic orbital overlap, one obtains

$$\langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} \hat{K}_i \mid \phi_j(1) \rangle = \sum_{i}^{\text{Occ.MOs}} C_{ij}C_{ii} \langle \phi_i\phi_i \mid \phi_j\phi_j \rangle$$

Since the bond order p_{ij} between i^{th} and j^{th} atoms is defined as

$$p_{ij} = 2 \sum_{i}^{\text{Occ.MOs}} C_{ij}C_{ii}$$

where each molecular orbital is doubly occupied, we have

$$\langle \phi_i(1) \mid \sum_{i}^{\text{Occ.MOs}} K_i \mid \phi_j(1) \rangle = \tfrac{1}{2}\, p_{ij} \langle \phi_i\phi_i \mid \phi_j\phi_j \rangle \qquad \text{(A8.6)}$$

The combination of Eqs. (A8.5) and (A8.6) gives Eq. (8.89), i.e.,

$$\beta_{ij} = \beta_{ij}\,(\text{core}) - \tfrac{1}{2}\, p_{ij} \langle \phi_i\phi_i \mid \phi_j\phi_j \rangle$$

PROBLEMS

1. Calculate the total π-electron energy and delocalisation energy in square cyclobutadiene. Show that its ground state is a triplet.
2. Show that in the lowest excited configuration (i.e. $\psi_1^2\psi_2^1\psi_3^1$) of butadiene the central bond is shorter than the end bonds while in butadiene-anion ($\psi_1^2\psi_2^2\psi_3^1$) the bond orders become nearly equal.
3. Establish the Woodward-Hoffmann rule for the inter-conversion of cyclopropyl cation to allyl cation and that of cyclopropyl anion to allyl anion.
4. Calculate the transition energies for transition from the ground state to the first excited singlet and the lowest triplet states of ethylene using the PPP approximation. The value of β for ethylene is -3.0 eV for the equilibrium bond length of 1.35 Å.
5. Find the energy levels and MO wavefunctions of benzene from Eqs. (8.60) and (8.61). Show from Hückel theory that the π-delocalisation energies in neutral, cation and anion of benzene are same.
6. Show that for unsaturated molecules $\sum_i q_i = n_\pi$ where n_π is the total number of π-electrons in the molecule. For definition of q_i see Eq. (8.26).

9

Symmetry

9.1 Introduction

Symmetry is a widely distributed property in nature. The human body is symmetric; the left hand side is the mirror image of the right hand side. Each wing of a butterfly is the mirror image of the other wing. Thus, a plane of symmetry divides the two halves and a reflection in this plane transfers the left hand side to the right hand side and vice versa. As this operation does not cause any change or deformation in the object, the result of the operation is indistinguishable from the original. Such operation is called the symmetry operation. There are essentially three fundamental types of symmetry operations—the ***rotation*** of the object through a definite angle about some axis, the ***reflection*** of it in some plane, and the ***translation*** of the object over some distance. Of these, the translation operation is applicable only to an infinite medium such as a crystal lattice. An object of finite dimensions, such as a molecule, can be symmetrical only with respect to rotations and reflections.

Symmetry operations in a molecule are carried out with respect to some fixed plane or a fixed axis. These features are called elements of symmetry. Consider the water molecule as shown in Fig. 9.1. A reflection in the *zy* plane merely interchanges the two hydrogen atoms without disturbing the oxygen atom. Similarly a rotation by 180° about the *z*-axis interchanges the two hydrogen atoms so that the result in each case is indistinguishable from the original molecule. Thus, the *zy* plane and the *z*-axis are the elements of symmetry. On the other hand, if a rotation by 180° is performed about the *x*- or *y*-axis [Fig. 9.1(c) and (d)] then the water molecule becomes distinguishable from the original in the space fixed coordinate system. Hence, the *x*- and the *y*-axes are not the elements of symmetry and the rotation by 180° about the *x*- or the *y*-axis is not the symmetry operation for the water molecule.

9.2 Various Types of Symmetry Operations

Although there are two fundamental types of symmetry operations, such as

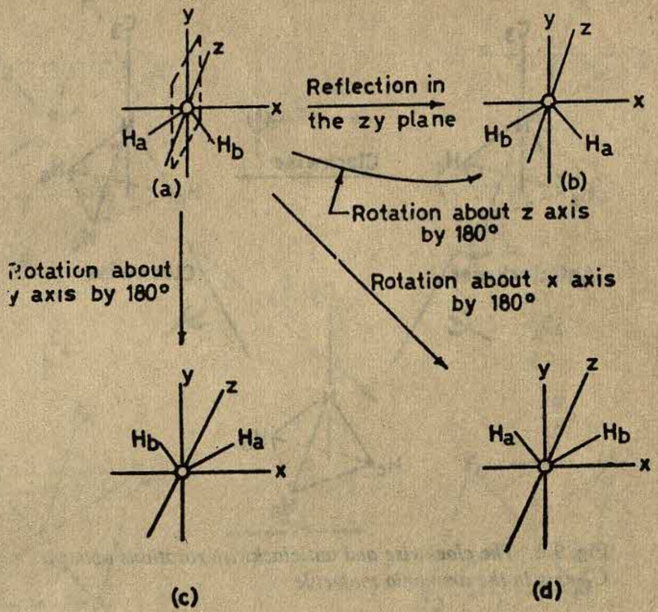

y
z
x
Ha
Hb
(a)
Reflection in the zy plane
(b)
Rotation about z axis by 180°
Rotation about y axis by 180°
Rotation about x axis by 180°
(c)
(d)

Fig. 9.1 *Symmetry operations in the water molecule*

rotation and reflection mentioned in Sec. 9.1, an examination of different molecules reveals that there are essentially four types of symmetry operations—rotations, reflections, improper rotations, and inversion—which will now be considered in detail.

Rotations

A rotation through $2\pi/n$ radians or $360°/n$ about an axis is denoted by C_n. Such an axis is called the n-fold axis of symmetry. The number n can take any integral value: $n = 1, 2, 3, 4$, etc. The value $n = 1$ corresponds to a rotation through an angle 2π, which means doing nothing on the molecule. In other words, C_1 means an identity operation E which leaves the molecule unmoved. The z-axis in the water molecule (Fig. 9.1) is a twofold axis of symmetry. A rotation through $2\pi/2$, i.e. 180° about this axis is called the C_2 operation.

Figure 9.2 shows an ammonia molecule that has a threefold axis of symmetry, C_3. Rotation about this axis by $2\pi/3$ (i.e. 120°) may be performed in a clockwise or anticlockwise direction. Whilst either operation restores the molecule to its original appearance neither result is identical with the original so far as the positions of the different hydrogen nuclei are concerned. The clockwise C_3 and anticlockwise C_3' rotations must therefore be regarded as two distinct examples of rotations about a threefold axis.

If, however, C_3 is performed twice, i.e., C_3^2, the molecule is then brought into a position identical to that which results from C_3' on the starting object (Fig. 9.2), i.e.

$$C_3 \times C_3 = C_3^2 = C_3' \tag{9.1}$$

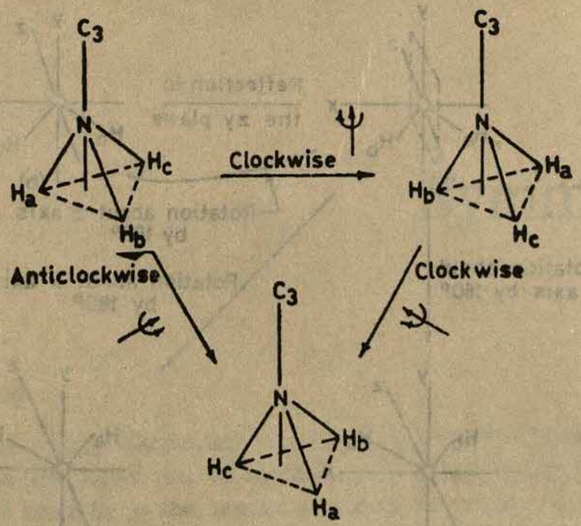


Fig. 9.2 *The clockwise and anticlockwise rotations about a C_3-axis in the ammonia molecule*

However, it may be noted that

$$C_3^3 = E = (C_3')^3 \tag{9.2}$$

Thus, a rotation in a clockwise manner could be expressed in terms of a rotation in an anticlockwise fashion or vice versa. It will be, therefore, advisable to consider all rotations as being performed in the same sense.

Figure 9.3 shows SF_6 (sulfur hexafluoride) that has a fourfold axis of symmetry which passes through F_5-S-F_6 atoms and is perpendicular to the plane of the other four fluorine atoms. It can be seen that successive C_4-operations (all clockwise) yield four different symmetry operations, C_4, C_4^2, C_4^3 and C_4^4. Note that

$$C_4^4 = E \tag{9.3}$$

$$C_4^2 = C_2 \tag{9.4}$$

The fivefold and sixfold axes of symmetry are seen in cyclopentadienyl anion $C_5H_5^-$ and benzene C_6H_6 respectively (Fig. 9.4).

Linear molecules, such as acetylene, hydrogen chloride, etc., have an infinite-fold axis (Fig. 9.5). A rotation through an indefinitely small angle θ about the internuclear axis gives rise to a conformation which is indistinguishable from the starting molecule. Such an operation which is denoted by C_∞ is a symmetry operation for diatomic and linear polyatomic molecules.

It should be noted here that a molecule may have two-, three- and four-fold axes of symmetry but the axis of n-fold rotation characterised by the largest n is called, by convention, the principal axis.

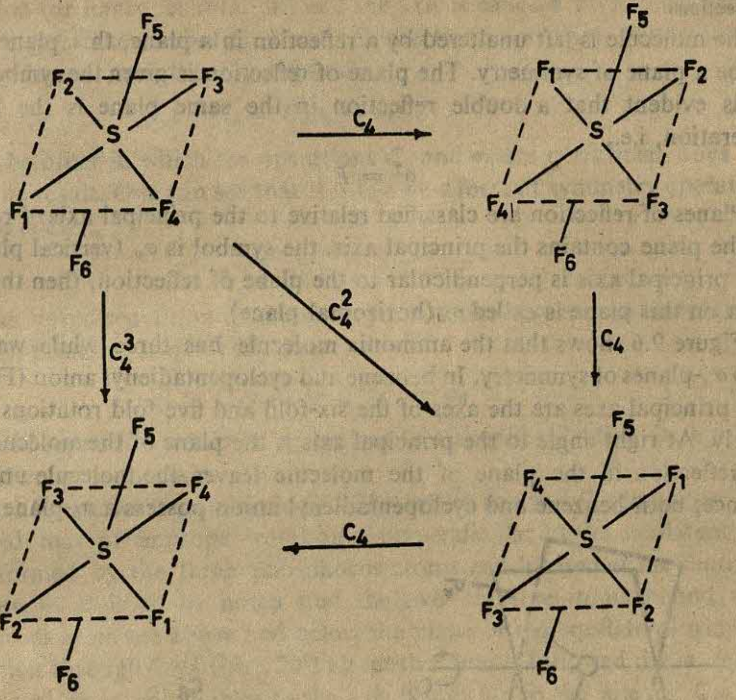


Fig 9.3 *Rotation in SF about a four-fold axis*

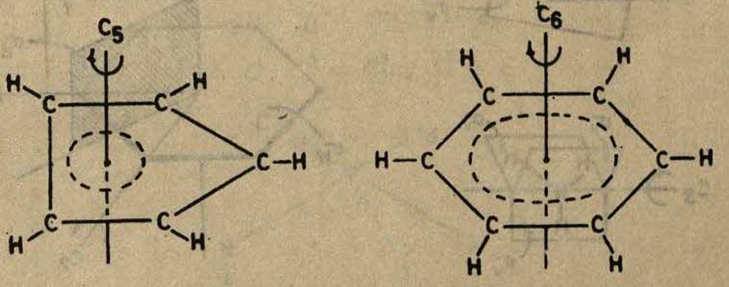


Fig. 9.4 *A five-fold and a six-fold axes in* $C_5H_5^-$ *and* C_6H_6 *respectively*

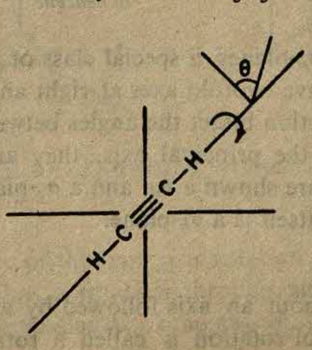


Fig. 9.5 *An infinite-fold axis in acetylene*

Reflections

If the molecule is left unaltered by a reflection in a plane, this plane is said to be a plane of symmetry. The plane of reflection is given the symbol σ and it is evident that a double reflection in the same plane is the identity operation, i.e.,

$$\sigma^2 = E \tag{9.5}$$

Planes of reflection are classified relative to the principal axis of rotation. If the plane contains the principal axis, the symbol is σ_v (vertical plane). If the principal axis is perpendicular to the plane of reflection, then the reflection on this plane is called σ_h (horizontal plane).

Figure 9.6 shows that the ammonia molecule has three while water has two σ_v-planes of symmetry. In benzene and cyclopentadienyl anion (Fig. 9.4), the principal axes are the axes of the six-fold and five-fold rotations respectively. At right angle to the principal axis is the plane of the molecule itself. A reflection in the plane of the molecule leaves the molecule unaltered. Hence, both benzene and cyclopentadienyl anion possess a σ_h-plane each.

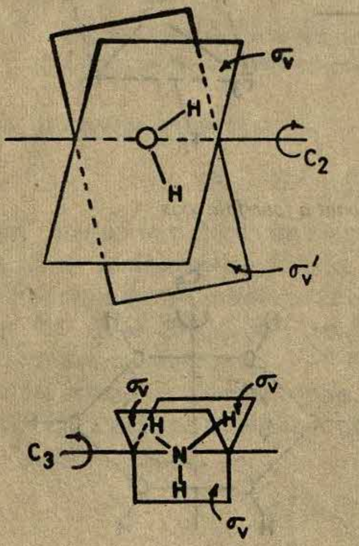


Fig. 9.6 *Two* σ_v- *and three* σ_v-*planes in* H_2O *and* NH_3 *respectively*

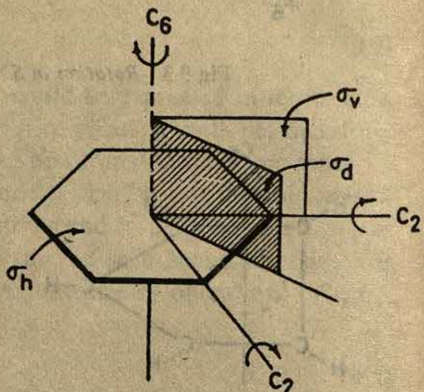


Fig. 9.7 *One* σ_v-, *one* σ_d- *and a* σ_h-*plane in benzene*

Besides the σ_v- and σ_h-planes, a special class of the σ_v-plane is found in some molecules that have twofold axes at right angles to the principal axis. If the planes of reflection bisect the angles between two adjacent two-fold axes and pass through the principal axis, they are called σ_d-plane (d for dihedral). In Fig. 9.7 are shown a σ_d- and a σ_v-plane in benzene while the plane of the molecule itself is a σ_h-plane.

Improper Rotations

A rotation by $2\pi/n$ about an axis followed by a reflection in a plane perpendicular to the axis of rotation is called a rotation-reflection symmetry operation (or improper rotation) and the axis is called a rotation-reflection axis and given the symbol S_n. If σ_h is a reflection in a plane perpendicular to the principal axis, then by definition

$$S_n = C_n\sigma_h = \sigma_h C_n \tag{9.6}$$

where the order in which the operations C_n and σ_h are performed does not affect the result. One can see that this is a new form of symmetry operation. When n is even,

$$S_n^n = C_n^n \cdot \sigma_h^n = E \times E = E \tag{9.7}$$

Thus, an n-fold repetition of the improper rotation returns the molecule to its initial position. If n is odd, then

$$S_n^n = C_n^n \times \sigma_n^n = E \times \sigma_h = \sigma_h \tag{9.8}$$

An n-fold repetition would be equivalent to a simple reflection in a plane perpendicular to the axis.

Figure 9.8 shows the molecule $(PNCl_2)_3$ which has the S_3-symmetry. The threefold axis of improper rotation is perpendicular to the equilateral triangle formed by the three phosphorus atoms and located at the centre of the triangle. It is to be noted that the two chlorine-atoms bound to a phosphorus atom are above and below the plane of the equilateral triangle. A rotation through $2\pi/3$ (i.e. 120°) about the S_3-axis followed by a reflection in a plane at right angles to the axis brings Cl_a to the site of Cl_b. At the same time, other Cl atoms have moved, i.e. $Cl_b \rightarrow Cl_c$, $Cl_c \rightarrow Cl_d$, etc., leaving the molecule unaltered. It can be shown that

$$S_3^2 = S_3 \times S_3 = C_3^2;\ S_3^3 = \sigma_h$$
$$S_3^4 = C_3;\ S_3^5 = C_3^2\sigma_h;\ S_3^6 = E \tag{9.9}$$

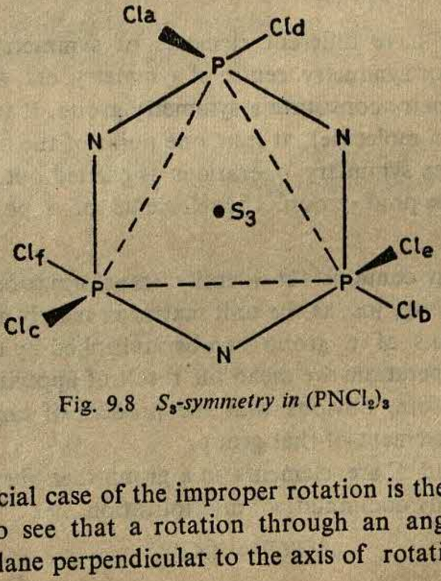


Fig. 9.8 S_3-*symmetry in* $(PNCl_2)_3$

Inversion

An important special case of the improper rotation is the inversion operation. It is easy to see that a rotation through an angle π followed by a reflection in the plane perpendicular to the axis of rotation is inversion. A molecule symmetrical with respect to this transformation is said to have a centre of symmetry. The operation of inversion is denoted by *i*, so that

$$i = S_2 = C_2\sigma_h \tag{9.10}$$

In Fig. 9.9 is shown that *trans*-dichloroethylene has a centre of symmetry while *cis* dichloroethylene does not. The action of inversion (i.e. *i*) on the *trans*-compound causes the atom Cl_a to move to Cl_b, H_d to H_c and C_e to C_f and vice versa and thus, reproduces the original molecule exactly. On the other hand, a similar action on the *cis*-compound causes the atom Cl_a to move to H_c and H_d to Cl_b and vice versa, and therefore this molecule is not symmetrical with respect to inversion.

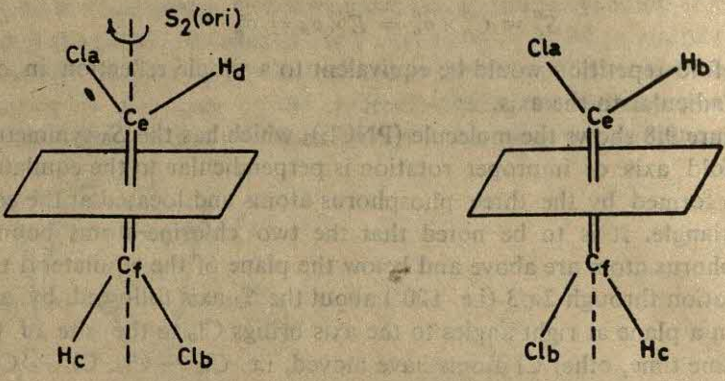


Fig. 9.9 *Symmetry operations in cis- and trans-dichloroethylene*

9.3 Point-Groups

A molecule may have different elements of symmetry such as axes of symmetry, planes of symmetry, centre of symmetry, etc. A collection of these elements of symmetry constitute a symmetry group. If in an object of finite dimensions (say, a molecule), at least one point of the object remains fixed when any of these symmetry operations is carried out, then the symmetry group is called the point-group. The elements of a point-group obey the following rules:

(1) Each group contains the identity transformation *E*, called the unit element of the group, just as the unit matrix in matrix algebra.

(2) The elements of a group can be multiplied by one another. By the product of two operations we mean the result of applying them in succession. It is, therefore, obvious that the product of any two elements of a group is also an element of that group.

(3) If *A*, *B* and *C* are elements in a group then they follow associative (but not necessarily commutative) multiplication, i.e.

$$A(BC) = (AB)C \tag{9.11}$$

If for all elements $AB = BA$, the group is said to be Abelian.

(4) For each element A, in a group there exists in the same group an inverse element A^{-1} which means undoing or reversing the operation represented by A. In other words, if A and A^{-1} are carried out in succession the net effect is the identity transformation, i.e.

$$AA^{-1} = A^{-1}A = E \tag{9.12}$$

We shall now enumerate some important point-symmetry groups.

C_n Groups

These are known as the cyclic groups. In the C_n groups the n-fold axis is the only symmetry operation besides the identity operation, i.e. E. Such groups contain n-symmetry elements as

$$C_n\, C_n^2\, C_n^3 \ldots C_n^n = E$$

Thus, C_1 is a point-group without any symmetry operation except E. C_2 is a group with one twofold axis of symmetry and has therefore the elements C_2 and E. Notice that $C_2^2 = E$, and $C_2^{-1} = C_2 \ldots$ so that the elements of the group C_2 obey all the four rules of a point-group. The C_3 group has the elements C_3, C_3^2 and $C_3^3 = E$. The C_6 group contains C_6, $C_6^2 = C_3$, $C_6^3 = C_2$, $C_6^4 = C_3^2$, C_6^5 and $C_6^6 = E$. One can show that all elements in a cyclic group commute with each other; hence a cyclic group is Abelian.

C_{nv} Groups

These groups are obtained from the C_n-groups by adding a vertical plane of symmetry, i.e. σ_v. The addition of one σ_v-plane may imply the presence of another operation if the set of operations has to satisfy the above four requirements of a point-group. Thus, in C_{2v} to which the water molecule belongs (Fig. 9.10), when the $C_2(z)$ and $\sigma_v(xz)$ operations are carried out in succession the net effect is also obtained by $\sigma_v'(yz)$ on the starting object.

In algebraic form this is written as

$$C_2(z)\sigma_v(zx) = \sigma_v'(yz)$$

This shows that the C_{2v} group possesses the elements E, $C_2(z)$, $\sigma_v(yz)$ and $\sigma_v'(yz)$. In Table 9.1 is given the group multiplication table for the C_{2v} group.

TABLE 9.1 *Group-multiplication Table for the C_{2v} Group*

	E	$C_2(z)$	$\sigma_v(zx)$	$\sigma_v'(yz)$
E	E	C_2	σ_v	σ_v'
$C_2(z)$	C_2	E	σ_v'	σ_v
$\sigma_v(zx)$	σ_v	σ_v'	E	C_2
$\sigma_v'(yz)$	σ_v'	σ_v	C_2	E

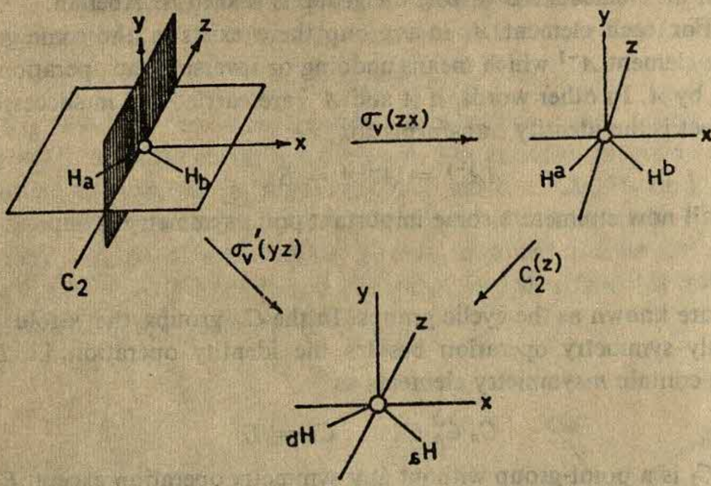


Fig. 9.10 *Effect of* σ_v- *and* C_2 *on* H_2O. *The subscripts 'a' and 'b' are added to emphasise the detailed effect of the operations*

Table 9.1 shows that for the C_{2v} group, the result is independent of the order in which the two operations are carried out. The elements of the group therefore commute and the group is Abelian.

We shall now examine a non-Abelian group, the C_{3v} group. Molecules like NH_3, PH_3, CH_3^-, etc., belong to this symmetry group. This group contains, besides the identity operation E, two rotation operators, i.e. C_3 and C_3^2, and three vertical planes of symmetry each of which contains one of the hydrogen nuclei (Fig. 9.6). If the three hydrogen atoms are labelled as H_a, H_b and H_c then the three σ_v-planes can be identified as σ_{va}, σ_{vb}, and σ_{vc}. It is seen in Fig. 9.11 that

$$C_3\sigma_{va} \neq \sigma_{va}C_3$$

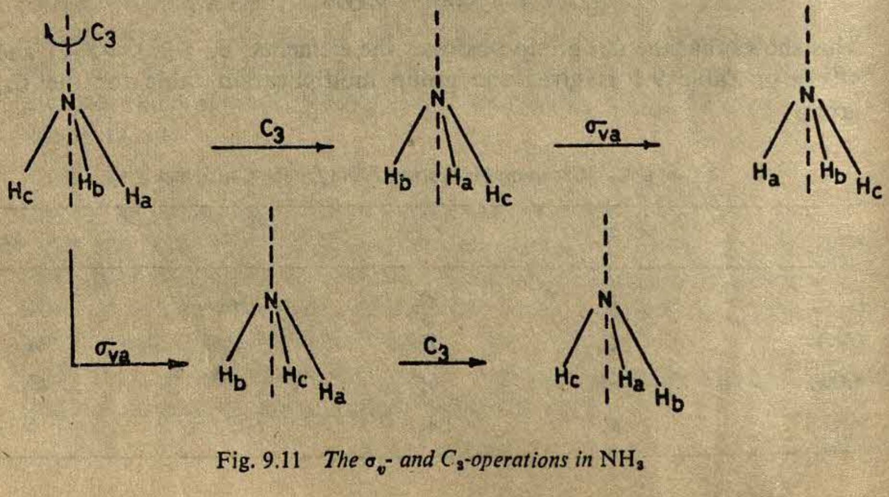


Fig. 9.11 *The* σ_v- *and* C_3-*operations in* NH_3

On the other hand, we find

$$C_3\sigma_{va} = \sigma_{vb}$$
$$\sigma_{va}C_3 = \sigma_{vc}$$

The group-multiplication for the C_{3v} group is shown in Table 9.2.

TABLE 9.2 *Group-multiplication Table for the C_{3v} Group*

Second operation	*First operation*					
	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
E	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
C_3	C_3	C_3^2	E	σ_{vc}	σ_{va}	σ_{vb}
C_3^2	C_3^2	E	C_3	σ_{vb}	σ_{vc}	σ_{va}
σ_{va}	σ_{va}	σ_{vb}	σ_{vc}	E	C_3	C_3^2
σ_{vb}	σ_{vb}	σ_{vc}	σ_{va}	C_3^2	E	C_3
σ_{vc}	σ_{vc}	σ_{va}	σ_{vb}	C_3	C_3^2	E

One can infer from the above multiplication table that each reflection operation is its own inverse, while $C_3^{-1} = C_3^2$.

The point-group $C_{\infty v}$ has an ∞-fold rotation axis and an infinite number of planes through this axis (Fig. 9.12).

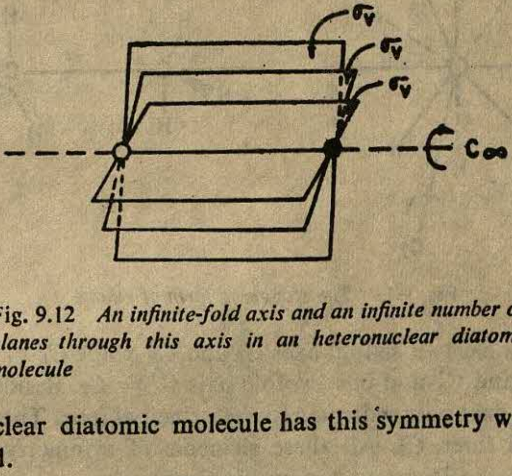


Fig. 9.12 *An infinite-fold axis and an infinite number of planes through this axis in an heteronuclear diatomic molecule*

A heteronuclear diatomic molecule has this symmetry with the C_∞ axis along the bond.

C_{nh} Groups

These groups contain the n-rotational operators and also the n-operators in which each rotation is multiplied, in turn, by σ_h, as

$$C_n, C_n^2, C_n^3, \ldots C_n^n = E, C_h\sigma_n = S_n, C_n^2\sigma_h, C_n^3\sigma_h \ldots \sigma_h$$

Thus, C_{1h} has the elements E and σ_h. The C_{2h} group has E, C_2, σ_h and i. An example of C_{2h} is *trans*-dichloroethylene (Fig. 9.9). A C_{nh} group, therefore, contains $2n$-elements. All the elements of such group commute and hence it is Abelian. When n is odd, the C_{nh} groups do not have the element i, while they do when n is even.

S_n Groups

The S_n-group has an S_n-axis as its basis. The presence of an n-fold rotation-reflection axis implies the presence of other symmetry operations. For example, an S_4 operation implies a presence of C_2 and $S_4^3 = S_4^{-1}$. Point-groups S_n are defined for even n. If n is even, then $S_n^n = C_n^n = E$, so there will be n symmetry operators but if n is odd then $S_n^n = C_n^n \times \sigma_h^n = \sigma_h$ and $S_n^{2n} = E$ and the group will then have $2n$-symmetry operators. Since S_n (n odd) has both σ_h and $C_n^x = S_n^{2x}$, it becomes identical with C_{nh} (n-odd).

D_n Groups (Dihedral Groups)

Such groups have n twofold axes, perpendicular to the principal n-fold axis. There is no plane of symmetry in this group. D_1 has the elements E and C_2 and is therefore identical with the C_2 group. D_2 has E, $C_2^{(x)}$, $C_2^{(y)}$ and $C_2^{(z)}$. D_3 has two threefold axes C_3 and C_3^2 and three twofold axes C_2 perpendicular to the C_3 axis. The staggered form of ethane has this symmetry (Fig. 9.13).

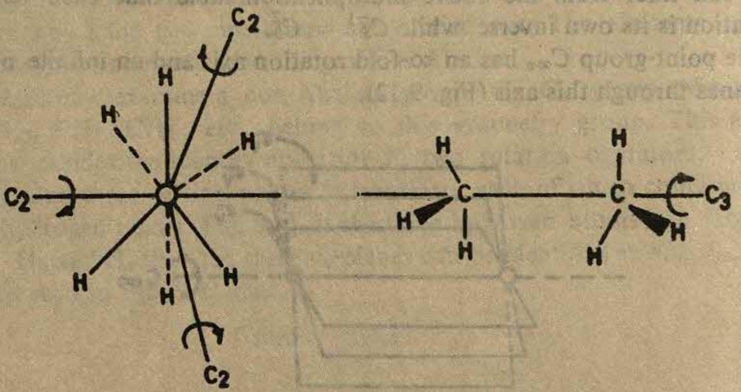


Fig. 9.13 *The staggered form of ethane*

The group D_6 has two sixfold axes C_6 and C_6^5 while $C_6^6 = E$, two threefold $C_6^2 = C_3$ and C_6^4 and one twofold axis $C_6^3 = C_2$. Besides the above, it has six twofold axes perpendicular to the principal axis. They are denoted by three C_2' and three C_2''. All these elements of symmetry are shown in Fig. 9.14. Thus, the D_6 group has twelve elements.

D_{nd} Groups

The addition of σ_d-operation to D_n groups yields the D_{nd} groups. The elements of D_2 are E, $C_2^{(x)}$, $C_2^{(y)}$ and $C_2^{(z)}$. The D_{2d} group will contain, in addition to the elements of

$$D_2,\ \sigma_d \times E,\ C_2^{(x)} \times \sigma_d = S_4,\ C_2^{(y)} \times \sigma_d = S_4^3, \text{ and } C_2^{(z)} \times \sigma_d = \sigma_d'.$$

An example of D_{2d} is allene, $H_2C = C = CH_2$.

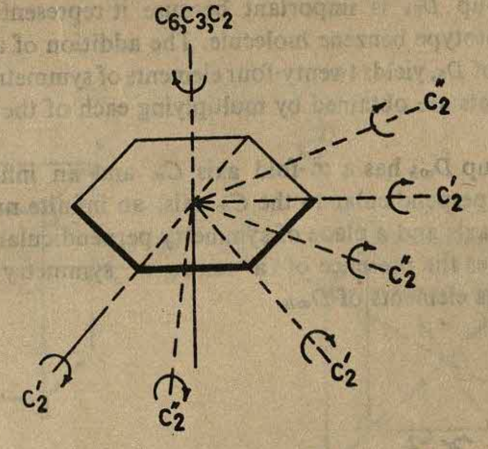


Fig. 9.14 *The various two-fold axes in a D_6 group*

D_{nh} Groups

The addition of a σ_h-plane to the set of elements of the D_n group yields D_{nh}.

D_{2h} is one of the very frequently occurring point groups among molecules. It is often called V_h. It has three mutually perpendicular two-fold axes, three mutually perpendicular planes of symmetry and as a consequence a centre of symmetry. Pyrazine is an example of D_{2h}. In Fig. 9.15 are shown the various elements of symmetry in the pyrazine molecule.

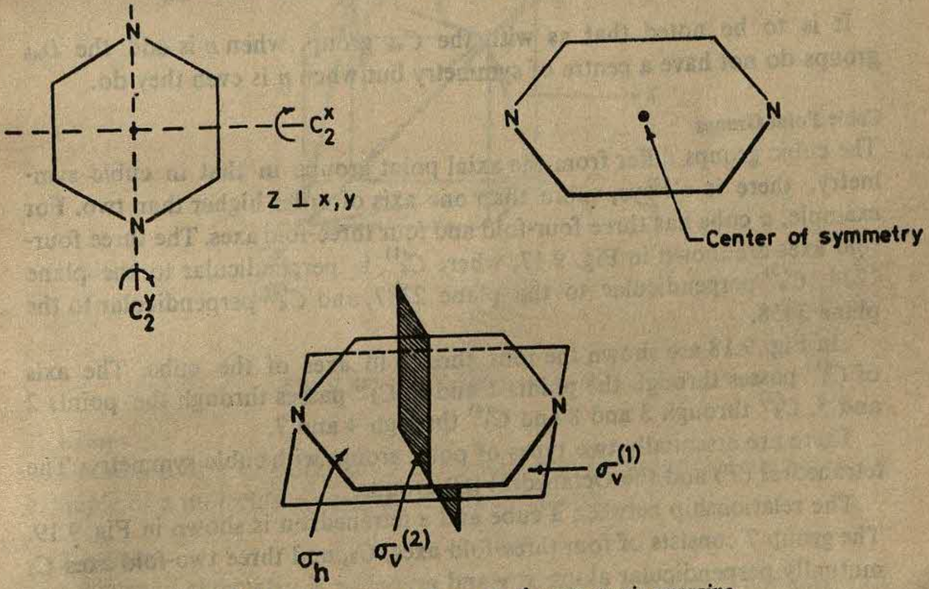


Fig. 9.15 *The various elements of symmetry in pyrazine*

The point group D_{3h} has one three-fold axis, C_3, three two-fold axes at right angles to the former and three planes of symmetry σ_v through it, as well as one σ_h plane perpendicular to σ_v but no centre of symmetry.

The point-group D_{6h} is important because it represents the symmetry group of the prototype benzene molecule. The addition of a σ_h-plane to the twelve elements of D_6, yields twenty-four elements of symmetry. The additional twelve elements are obtained by multiplying each of the twelve elements of D_6 by σ_h.

The point group $D_{\infty h}$ has a ∞-fold axis C_∞ and an infinite number of twofold axes C_2 perpendicular to the C_∞ axis, an infinite number of planes through the C_∞ axis and a plane of symmetry perpendicular to the C_∞ axis which also implies the presence of a centre of symmetry *i*. Figure 9.16 shows the various elements of $D_{\infty h}$.

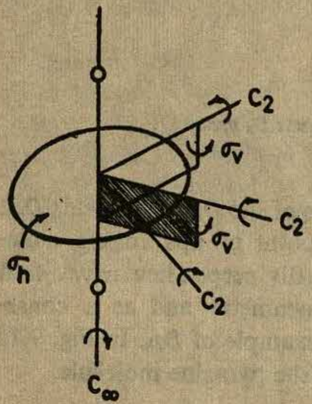


Fig. 9.16 *The various elements of* $D_{\infty h}$

It is to be noted that as with the C_{nh} group, when *n* is odd, the D_{nh} groups do not have a centre of symmetry but when *n* is even they do.

Cubic Point Groups

The cubic groups differ from the axial point groups in that in cubic symmetry, there is always, more than one axis of order higher than two. For example, a cube has three four-fold and four three-fold axes. The three four-fold axes are shown in Fig. 9.17, where $C_4^{(1)}$ is perpendicular to the plane 1234, $C_4^{(2)}$ perpendicular to the plane 2387, and $C_4^{(3)}$ perpendicular to the plane 3458.

In Fig. 9.18 are shown the four three-fold axes of the cube. The axis of $C_3^{(1)}$ passes through the points 1 and 6, $C_3^{(2)}$ passes through the points 2 and 5, $C_3^{(3)}$ through 3 and 8 and $C_3^{(4)}$ through 4 and 7.

There are essentially two types of point groups with cubic symmetry: The tetrahedral (*T*) and the Octahedral (*O*) groups.

The relationship between a cube and a tetrahedron is shown in Fig. 9.19. The group *T* consists of four three-fold axes, C_3, and three two-fold axes C_2 mutually perpendicular along *x*, *y* and *z*.

One can show that the elements C_3 and C_3^2 are two different operations (Fig. 9.20) while $C_3^3 = E$. There are therefore four C_3^2 operations in the group *T*.

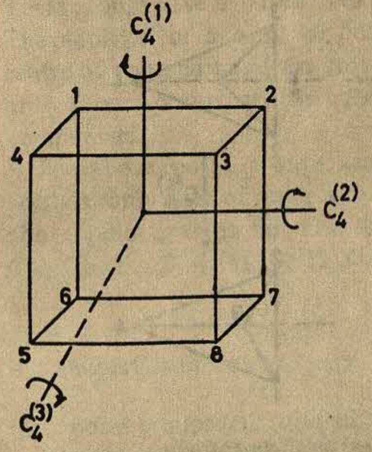


Fig. 9.17 *The three four-fold axes in a cube*

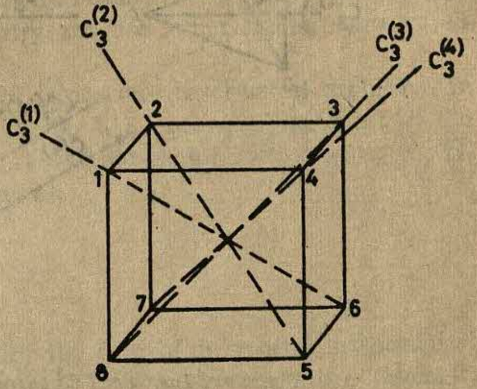


Fig. 9.18 *The four three-fold axes in a cube*

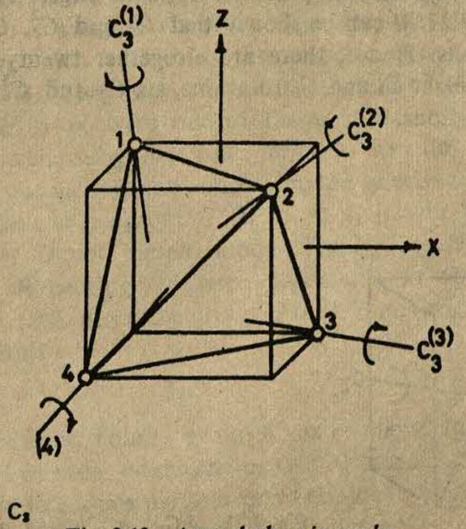


Fig. 9.19 *A tetrahedron in a cube*

T_d Groups

The addition of a σ_d-plane to T generates the T_d group. Methane is an example of a molecule possessing the T_d symmetry.

$T_i(T_h)$ Groups

If a centre of symmetry is added to T the T_i group is formed. The elements of T_i are those of T and also each of those operators multiplied by i.

O Groups

The system of axes of the octahedron group is that of a cube. There are three fourfold axes, C_4, which pass through the centres of opposite faces (see

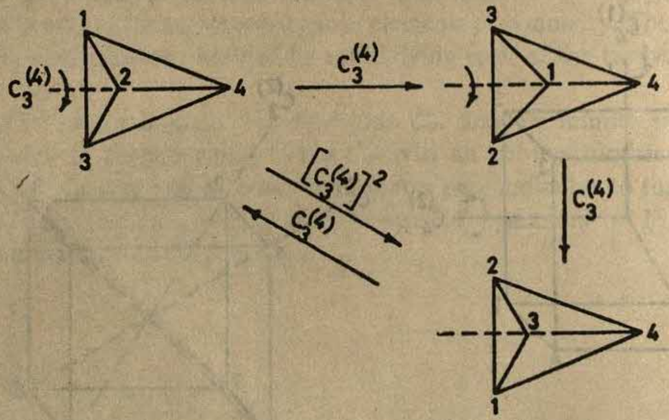


Fig. 9.20 *The* C_3 *and* C_3^2 *operations on a tetrahedron*

Fig. 9.17), four three-fold axes through opposite corners (Fig. 9.18) and six two-fold axes through the midpoints of opposite edges. The system of axes is shown in Fig. 9.21. It can be shown that C_3 and C_3^2, $C_4C_4^2$ and C_4^3 are different operations. Hence, there are altogether twenty-four elements in the group O : E, eight C_3 and C_3^2 rotations, six C_4 and C_4^3 rotations, three C_4^2 and six C_2 rotations.

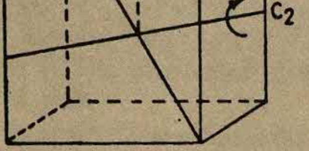


Fig. 9.21 *A* C_3-, *a* C_4- *and a* C_2-*axes in a cube*

O_h Groups

This group is generated from O by adding a centre of symmetry. Thus, the three-fold axes in the group O are converted into rotatory-reflection axes of the sixth order. In addition, another six planes of symmetry appear passing through each pair of opposite edges and three planes parallel to the faces of the cube. Thus the group O_h contains 48 elements. Both the cube and the regular octahedron have this symmetry. Numerous octahedral coordination complexes are examples of this point group:

SiF_6^{-2}, SF_6, $PbCl_6^{-6}$, $Fe(CN)_6^{-4}$, $Mo(CO)_6$, etc.

I Groups (Icosahedral)

These groups have five-fold axes in addition to three-fold and two-fold axes. The addition of a σ_h-plane perpendicular to the two-fold axes leads to a centre of symmetry and the group is then called the I_h group. Such groups are of rare occurrence in chemistry and are found among some boron compounds.

The above point groups are of importance in chemical problems. In crystals, only axes of order $n = 1, 2, 3, 4, 6$ occur, so that most of the above point groups fall into the 32 crystallographic point groups; C_n, S_n, C_{nv}, C_{nh}, D_n, D_{nd}, D_{nh}, T, T_d, O and O_h.

9.4 Properties of Point-Groups

The point-groups are studied with the help of the general mathematical technique called group theory. Let G be some group with g elements. Suppose, some set of elements, say $H_1, H_2, \ldots, H_h$ which are present in G are found to obey the four rules of a point-group (see Sec. 9.3). Then, these set of elements $H_1, H_2, \ldots H_h$ form a subgroup H. The number of elements in a group or subgroup is called the order. Now take an element F, of the group G, which is absent in the subgroup H and form the products $FH_1, FH_2, \ldots FH_h$. They must all be in the group G but not in the subgroup H. If $FH_i = H_j$ were one of the members of H then $F = H_jH_i^{-1}$ should also be in the subgroup H according to the rules (see Sec. 9.3). This is contrary to our assumption concerning the selection of F. We have thus found $2h$ members of the group G. If $2h < g$, it will be possible to find another element D not present among $H_1, H_2, \ldots H_h$ nor among $FH_1, FH_2, \ldots FH_h$. Repeating the same arguments we obtain h new elements $DH_1, DH_2, \ldots DH_h$. Since the group G is of finite order, i.e. g, this procedure will end until

$$kh = g \tag{9.13}$$

where k is an integer. Thus, a group of six elements, for example, can only have subgroups of order either one or two or three.

We shall now introduce the concept of conjugate elements. Two elements, say A and B, of a group are said to be conjugate if

$$A = X^{-1}BX \tag{9.14}$$

where X is another element of the same group. Such transformation is known as similarity transformation. If we multiply A on its left by X and on its right by X^{-1} and do the same on the right hand side of Eq. (9.14), we have

$$XAX^{-1} = XX^{-1}BXX^{-1} \tag{9.15}$$

Since $XX^{-1} = E$, one may write Eq. (9.15) as

$$XAX^{-1} = B \tag{9.16}$$

In other words, the conjugate property of A and B is mutual. A complete set of elements, such as A, B, C, . . . etc. of a group, which are mutually conjugate with each other, is called a class. Each class is completely determined by any one element of it. For example, if an element A of a group is known we obtain the whole class by forming the product XAX^{-1} where X is successively every element of the group. The unit element E of any group is a class by itself, since for every other element of the group $XEX^{-1} = E$. It is important to note that a class of a group is not a subgroup because a class does not have to contain a unit element.

We can now show that the C_{3v} group which has six elements (see Table 9.2) has three classes of operations. The identity operation E is a class by itself. That C_3 and C_3^2 form a class can be shown by examining their similarity transformation (Eq. 9.14) with every other element of the group (see Fig. 9.11 and Table 9.2).

$$E^{-1}C_3E = EC_3E = C_3$$

$$C_3^{-1}C_3C_3 = C_3^2C_3C_3 = C_3^2C_3^2 = C_3$$

$$(C_3^2)^{-1}C_3C_3^2 = C_3C_3C_3^2 = C_3C_3^3 = C_3E = C_3$$

$$\sigma_{va}^{-1}C_3\sigma_{va} = \sigma_{va}C_3\sigma_{va} = \sigma_{va}\sigma_{vc} = C_3^2$$

$$\sigma_{vb}^{-1}C_3\sigma_{vb} = \sigma_{vb}\sigma_{va} = C_3^2$$

$$\sigma_{vc}^{-1}C_3\sigma_{vc} = \sigma_{vc}\sigma_{vb} = C_3^2$$

Similarly, the similarity transformation of C_3^2 by E, C_3 and C_3^2 gives C_3^2 and by σ_{va}, σ_{vb} and σ_{vc} gives C_3. Therefore, C_3^2 and C_3 are conjugate and the members of the same class. In an exactly same manner, the three σ_v-planes can be shown to belong to a class. The three classes of the C_{3v} group are as follows:

$$E,\ (C_3 \text{ and } C_3^2),\ (\sigma_{va}, \sigma_{vb}, \sigma_{vc})$$

They can be written as E, $2C_3$, $3\sigma_v$.

We shall now introduce the concept of isomorphism. Two groups G and G' of the same order are said to be isomorphous if we can establish a one to one correspondence between their elements such that, if the element A of the group G corresponds to the element A' of G', and B of G to B' of G', then AB corresponds to $A'B'$. Two such groups have identical properties though the actual meaning of their elements may be different.

9.5 How to Determine the Point-Group of a Molecule?

The first stage in the application of the theory of symmetry in a molecular problem is to establish the symmetry point-group to which the molecule belongs. In order to establish the point-group the following rules are important.

(1) There are three special groups which do not have any unique axis of high symmetry. They are tetrahedron, T_d (e.g. CH_4), the octahedron. O_h (e.g., $Fe(CN)_6^{-4}$) and icosahedron, I_h (e.g., boron compounds, $B_6H_{12}^{-2}$).

(2) If a molecule does not belong to any of the special groups, we look for an axis of symmetry. If it has none, it may have a mirror plane (C_{1h}) or a centre of symmetry (S_2). If it has no symmetry at all, the point group is C_1.

(3) If the molecule has axes of rotation, C_n, locate the axis of the highest order. This will be the principal axis. Sometimes there may be no unique principal axis but instead three mutually perpendicular C_2 axes (e.g., naphthalene). In this case one of these axes is arbitrarily chosen as the principal axis.

(4) If the molecule has the axis of improper rotation S_n where n is twice the order to the principal axis, then the group is S_n provided there is no other symmetry element except perhaps an inversion.

(5) Next, look for n twofold axes of symmetry perpendicular to the principal n-fold axis. If these are present the group is D, if not, it is C.

There are three types of the D-groups: (a) If there is no mirror plane, the group is D_n (D_2: twisted ethylene), (b) If the mirror plane is perpendicular to the principal axis, the point group will be D_{nh} (e.g. D_{6h}: benzene), (c) If there is no σ_h plane but there are planes that contain the principal axis and also bisect the angle between any two of the n-fold axes perpendicular to the principal axis (i.e. σ_d plane) then the point group will be D_{nd}.

There are also three types of the C-groups:

(a) If there is no plane of symmetry the group is C_n,
(b) If there are σ_v-planes, the group is C_{nv} (C_{3v}: ammonia),
(c) If there is a horizontal plane, the group is C_{nh}.

(6) Linear molecules belong to infinite or continuous point-groups which are of two kinds: $C_{\infty v}$ has no *centre* of symmetry (e.g. HCN, HCl). $D_{\infty h}$ has a *centre* of symmetry (e.g. CO_2, O_2, N_2).

9.6 Representations of Groups

Let us consider the C_{2v} group to which the water molecule belongs. There are four symmetry operators in the C_{2v} group, i.e. E, $C_2(z)$, $\sigma_v(xz)$, $\sigma_v'(yz)$ (Fig. 9.22).

Consider the effect of the various operations on the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals of the oxygen atom. They are as follows:

$$E\,2s = 2s, \quad C_2(z)2s = 2s, \quad \sigma_v(xz)2s = 2s, \quad \sigma_v'(yz)2s = 2s$$

$$E2p_x = 2p_x, \; C_2(z)2p_x = -\,2p_x,$$

$$\sigma_v(xz)2p_x = 2p_x. \; \sigma_v'(yz)2p_x = -\,2p_x$$

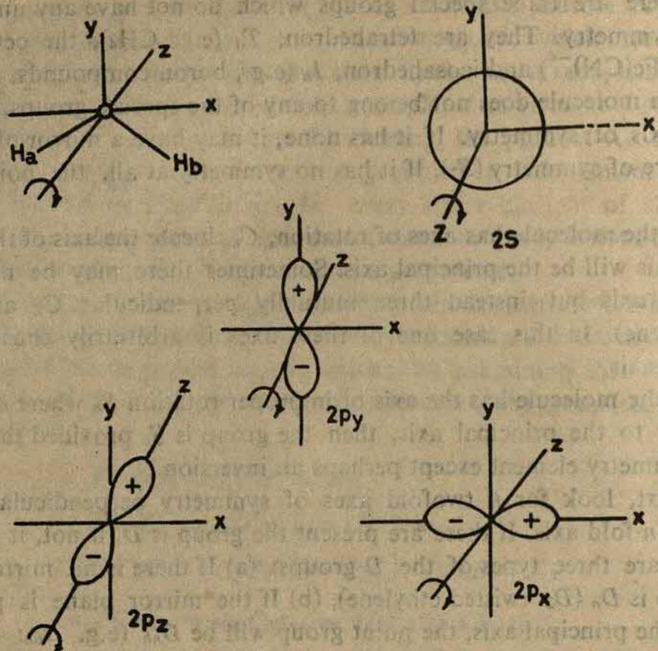


Fig. 9.22 *One 2s- and three 2p-orbitals of oxygen in* H_2O

$$E2p_y = 2p_y,\ C_2(z)2p_y = -\ 2p_y,$$

$$\sigma_v(xz)2p_y = -\ 2p_y,\ \sigma_v'(yz)2p_y = 2p_y$$

$$E2p_z = 2p_z,\ C_2(z)2p_z = 2p_z,$$

$$\sigma_v(xz)2p_z = 2p_z,\ \sigma_v'(yz)2p_z = 2p_z$$

Thus, we see that the effect of the various operators in this case is to restore the orbital to its original position either with or without a change of sign. This is same as multiplying the orbital by −1 or by +1. When the orbital is multiplied by +1, the orbital is said to be symmetric and when it is multiplied by −1, it is antisymmetric with respect to the operation in question. In other words, the effect of operators of the C_{2v} group on the oxygen orbitals can be summarised by the following set of numbers (Table 9.3).

TABLE 9.3 *Effect of Operators of* C_{2v} *on the Oxygen Orbitals*

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
$2s$	1	1	1	1	Γ_1
$2p_x$	1	−1	1	−1	Γ_2
$2p_y$	1	−1	−1	1	Γ^3
$2p_z$	1	1	1	1	Γ_4

Thus, each orbital is characterised by a set of numbers. The orbitals $2s$ and $2p_z$ are characterised by the set of four numbers $+1, +1, +1, +1$ which means that these two orbitals are totally symmetric in the C_{2v} group. According to the group multiplication table (Table 9.1) we see that $\sigma_v\sigma_v' = C_2$, then if an orbital is symmetric under σ_v and antisymmetric under σ_v' it must be antisymmetric under C_2. This is shown above by the behaviour of the $2p_x$ and $2p_y$ orbitals.

Any set of numbers which multiply according to the group multiplication table is said to form a representation of the group. A representation is denoted by Γ and Table 9.3 shows three representations of the C_{2v} group because Γ_1 and Γ_4 are the identical set of numbers. There may be sets of matrices which satisfy the group multiplication table. For example, if the various operations of C_{2v} are carried out on the two hydrogen $1s$ orbitals, H_a and H_b, we can generate the following set of two-dimensional matrices (Fig. 9.22).

$$E\begin{pmatrix} H_a \\ H_b \end{pmatrix} = \begin{pmatrix} (+1)H_a + (0)H_b \\ (0)H_a + (+1)H_b \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} H_a \\ H_b \end{pmatrix}$$

$$C_2(z)\begin{pmatrix} H_a \\ H_b \end{pmatrix} = \begin{pmatrix} (0)H_a + (+1)H_b \\ (+1)H_a + (0)H_b \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} H_a \\ H_b \end{pmatrix}$$

$$\sigma_v(xz)\begin{pmatrix} H_a \\ H_b \end{pmatrix} = \begin{pmatrix} (+1)H_a + (0)H_b \\ (0)H_a + (+1)H_b \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} H_a \\ H_b \end{pmatrix}$$

$$\sigma_v(yz)\begin{pmatrix} H_a \\ H_b \end{pmatrix} = \begin{pmatrix} (0)H_a + (+1)H_b \\ (+1)H_a + (0)H_b \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} H_a \\ H_b \end{pmatrix}$$

The set of matrices,

$$\begin{array}{cccc} E & C_2 & \sigma_v(xz) & \sigma_v'(yz) \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{array}$$

satisfy the group multiplication rule of the C_{2v} group. For example

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\text{i.e. } \sigma_v\sigma_v' = C_2$$

Hence, the above set of matrices forms a representation of the C_{2v} group. The set of numbers in Table 9.3 shows the special case where the matrices are one-dimensional.

The representation of a group is, therefore, a set of matrices which express mathematically the operation of a group on a function or a set of functions. Thus we can see that it is possible to generate as many representations as we like depending on the particular set of functions initially chosen; but there are, however, only a finite number of representations that have a special significance. These representations are called irreducible representations. It is possible to draw an analogy between a representation and a vector. In a three-dimensional space, one can imagine infinite number of vectors but each such vector can be expressed as a linear combination of only three orthogonal vectors. Similarly, for a finite group, any representation of the set of numerous representations can be expresssd in terms of the finite number of the irreducible representation as

$$\Gamma = C_1\Gamma^{(1)} + C_2\Gamma^{(2)} + C_3\Gamma^{(3)} + \ldots C_n\Gamma^{(n)} \tag{9.17}$$

where $C_1, C_2, \ldots$ are either positive integers or zero, $\Gamma^{(i)}$ is the i^{th} irreducible representation.

The method of breaking down a representation is by means of a similarity transformation. Suppose a representation of a finite group has been found, consisting of matrices (A), (B), (C), (D), each matrix being of dimension n. If there is a similarity transformation by a matrix X such that

$$\begin{aligned} X^{-1}AX &= \begin{bmatrix} A_1 & 0 \\ 0 & A_2 \end{bmatrix} \\ X^{-1}BX &= \begin{bmatrix} B_1 & 0 \\ 0 & B_2 \end{bmatrix} \text{ etc.} \end{aligned} \tag{9.18}$$

where $A_1, B_1 \ldots$ are of dimension $m(m < n)$ and $A_2, B_2, \ldots$ are of dimension $(n - m)$, then the matrices A, B, etc., are said to be reduced. If A_1, B_1, etc., and A_2, B_2, etc., cannot be reduced further by a similarity transformation, then these sets of matrices form the irreducible representations.

A criterion for reducibility or irreducibility of a matrix representation is provided by Schur's lemma. It says that, if there exists a non-constant matrix, i.e. one, which is not a simple multiple of the unit matrix, that commutes with all the matrices of a representation then the representation is reducible.

Let the set of matrices $E, A_1, A_2, \ldots A_n$ form a representation of a group with E being the identity matrix. Let M be a Hermitian matrix which commutes with every matrix of the representation, i.e.

$$MA_i = A_iM \tag{9.19}$$

Any Hermitian matrix can be diagonalised by a similarity transformation. Let us assume that the diagonal matrix is D and the transformation matrix is X, then

$$D = X^{-1}MX \tag{9.20}$$

Equation (9.19) may be written as

$$MXX^{-1}A_i = A_iXX^{-1}M \tag{9.21}$$

Since the matrix equation is not affected by a similarity transformation, we may write Eq. (9.21) as

$$X^{-1}(MXX^{-1}A_i)X = X^{-1}(A_iXX^{-1}M)X$$

or $$(X^{-1}MX)(X^{-1}A_iX) = (X^{-1}A_iX)(X^{-1}MX)$$

or
$$DA'_i = A'_iD \tag{9.22}$$
where the similarity transformation of A_i with X is A'_i. Thus every matrix $A'_1, A'_2, \ldots A'_n$ of the representation commutes with a particular diagonal matrix D. The matrix equation (9.22) can be expanded as

$$\begin{bmatrix} D_{11} & 0 & 0 & 0\ldots \\ 0 & D_{22} & 0 & 0\ldots \\ 0 & 0 & D_{33} & \ldots \end{bmatrix} \begin{bmatrix} A'_{11} & A'_{12},\ldots \\ A_{21} & A_{22},\ldots \\ \ldots & \ldots\ldots \end{bmatrix}$$

$$= \begin{bmatrix} A'_{11} & A'_{12},\ldots & \\ A'_{21} & A'_{22} & \\ \ldots & \ldots & \ldots \end{bmatrix} \begin{bmatrix} D_{11} & 0\ldots\ldots\ldots & \\ 0 & D_{22}\ldots\ldots\ldots & \\ 0 & 0 & D_{33}\ldots \end{bmatrix}$$

or
$$\begin{bmatrix} D_{11}A'_{11} & D_{11}A'_{12}\ldots \\ D_{22}A'_{21} & D_{22}A'_{22}\ldots \\ \ldots & \ldots \end{bmatrix} = \begin{bmatrix} A'_{11}D_{11} & A'_{12}D_{22}\ldots \\ A'_{21}D_{11} & A'_{22}D_{22}\ldots \\ \ldots & \ldots \end{bmatrix} \tag{9.23}$$

Under two conditions, Eq. (9.23) is valid:

1. $D_{11} = D_{22} = D_{33} = \ldots$ in which case the matrix D is a constant matrix. Or

2. All the off-diagonal elements of A', i.e. A'_{12}, A'_{21}, etc., are zero, in which case the matrices $A_1, A_2, \ldots A_n$ are reducible. The matrices A_i are reduced by a similarity transformation with a matrix X which also brings the commuting matrix M into diagonal form. Thus, the A'_i consist of nonzero diagonal elements and zero block diagonal entries such as in Eq. (9.18).

For an Abelian Group (such as C_{2v}) every element commutes with every other element. Thus such group must be represented by diagonal matrices since only sets of diagonal matrices will, in general, commute. *The representations must be one-dimensional* because a set of diagonal matrices of dimension greater than one will commute with a nonconstant diagonal matrix, in which case the representation will be reducible according to Schur's lemma.

9.7 The Character

The sum of the diagonal elements of a square matrix is called the character and is denoted by the symbol χ. The character of a matrix is not altered by similarity transformations. For example,
$$X^{-1}AX = B \tag{9.24}$$

If B is a $n \times n$ matrix, then
$$\chi_B = \sum_{i=1}^{n} B_{ii} \tag{9.25}$$

where B_{ii} is a diagonal element.

$$\chi_B = \sum_{i=1}^{n} B_{ii} = \sum_{i}^{n}\sum_{j}^{n}\sum_{k}^{n} X_{ij}^{-1} A_{jk} X_{ki} \tag{9.26}$$

Since the matrix elements are scalar numbers, their order of multiplication will not matter. Hence, we write Eq. (9.26) as

$$\begin{aligned}\chi_B &= \sum_{k}^{n}\sum_{i}^{n}\sum_{j}^{n} X_{ki} X_{ij}^{-1} A_{jk} \\ &= \sum_{k}^{n}\sum_{j}^{n} \delta_{kj} A_{jk} = \sum_{k}^{n} A_{kk} = \chi_A\end{aligned} \tag{9.27}$$

where δ_{kj} is Kronecker's delta such that

$$\begin{aligned}\delta_{kj} &= 0 \quad k \neq j \\ &= 1 \quad k = j\end{aligned} \tag{9.28}$$

Therefore, the matrices that correspond to the operators belonging to the same class in a group have the same characters.

9.8 Some Important Theorems Concerning the Irreducible Representations and Their Characters

If two irreducible representations differ only by a similarity transformation they are said to be equivalent. The nonequivalent irreducible representations are an important characteristic of a group and play a fundamental role in all quantum mechanical applications of group theory. We shall now list, without proof, some important theorems concerning the irreducible representations and the characters of the matrices that form the representations.

I. The number of irreducible representations is equal to the number of classes of the group.

II. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group, i.e.

$$l_1^2 + l_2^2 + l_3^2 + \ldots l_n^2 = h \tag{9.29}$$

where l_i is the dimension of the i^{th} irreducible representation, Γ_i and h is the order of the group.

III. The matrix elements of any two non-equivalent irreducible representations Γ_i and Γ_j satisfy the orthogonality relation

$$\begin{aligned}&\sum_{R} \Gamma_i(R)_{mn}\sqrt{(l_i/h)}\,\Gamma_j(R)_{pq}\sqrt{(l_j/h)} \\ &= \delta_{ij}\delta_{mp}\delta_{nq}\end{aligned} \tag{9.30}$$

where R is an element of the group, l_i and l_j are the dimensions of Γ_i and Γ_j. It is to be noted that $\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ otherwise.

Equation (9.30) covers three different cases:

(a) If Γ_i and Γ_j are different, $\delta_{ij} = 0$ then

$$\sum_{R} \Gamma_i(R)_{mn}\Gamma_j(R)_{pq} = 0 \tag{9.31}$$

(b) If Γ_i and Γ_j are the same, $\delta_{ij} = 1$, but $m \neq p$ and $n \neq q$ then

$$\sum_R \Gamma_i(R)_{mn}\Gamma_i(R)_{pq} = 0 \tag{9.32}$$

(c) If $i = j$, $m = p$, $n = q$, then

$$\sum_R \Gamma_i(R)_{mn}\Gamma_i(R)_{mn} = h/l_i \tag{9.33}$$

We, therefore, see from the above relations that the matrix components $\Gamma_i(R_1)_{mn}$, $\Gamma_i(R_2)_{mn}$, . . . $\Gamma_i(R_h)_{mn}$ of the h elements of the group can be regarded as the components of an h-dimensional vector which is orthogonal to anyone of the vectors obtained by a different choice of the subscripts m and n, as well as orthogonal to any of the similar vectors obtained from a different irreducible representation of the same group. If there are n such irreducible representations, each of dimension l_n, there are $l_1^2 + l_2^2 + \ldots l_n^2$ such orthogonal vectors. But it is possible to construct only h orthogonal vectors in an h-dimensional space. Hence

$$l_1^2 + l_2^2 + \ldots l_n^2 = h$$

Thus Eq. (9.29) follows directly from Eq. (9.30).

IV. Let us consider the relation

$$\sum_R \Gamma_i(R)_{mm}\Gamma_j(R)_{pp} = (h/l_j)\delta_{ij}\delta_{mp} \tag{9.34}$$

Summing over m from 1 to l_i and over p from 1 to l_j, one gets

$$\begin{aligned} \sum_R \chi_i(R)\chi_j(R) &= (h/l_j)\delta_{ij} \sum_{m=1}^{l_i} \sum_{p=1}^{l_j} \delta_{mp} \\ &= (h/l_j)\delta_{ij} \sum_{p=1}^{l_i} 1 = h\delta_{ij} \end{aligned} \tag{9.35}$$

If $i = j$, we have

$$\sum_R |\chi_i(R)|^2 = h \tag{9.36}$$

Thus, we see that the characters of the matrices of the irreducible representations form sets of orthogonal vectors and the length of each such vector is $h^{1/2}$. We also notice that the relation (9.36) can be used as a criterion of the reducibility of a representation. For a reducible representation the sum in Eq. (9.36) is always greater than h.

Equation (9.35) can be used to decompose any reducible representation into irreducible ones. Let $\chi(R)$ be the character of an operation R of a reducible representation. Then

$$\chi(R) = \sum_i a_i\chi_i(R) \tag{9.37}$$

where a_i is the number of times the i^{th} irreducible representation occurs in the reducible representation. Multiplying each side by $\chi_j(R)$ and summing over R one obtains from Eq. (9.35)

$$\sum_R \chi(R)\chi_j(R) = \sum_i \sum_R a_i\chi_i(R)\chi_j(R) = a_jh \tag{9.38}$$

So that

$$a_j = \frac{1}{h} \sum_{R} \chi(R)\chi_j(R) \tag{9.39}$$

9.9 Character Table for Point Groups

For most chemical applications, it is sufficient to know only the characters for each of the symmetry classes of a group. A character table is a collection of such data for all irreducible representations of the group. A few character tables for some common point groups that are used in chemistry are given in Appendix 9. A character table for any group can be obtained by application of the four important theorems I–IV discussed in Sec. 9.8, along with the knowledge of the complete multiplication table for the group. The labelling of the irreducible representations is done according to the following general rules on nomenclature:

(1) A and B are used to label irreducible representations of dimension 1, E and T to label those of dimension 2 and 3 respectively (sometimes F is used instead of T). The nomenclature E here should not be confused with the identity operation.

(2) A is used when the character for the rotation about the principal n-fold axis is $+1$ and B when it is -1. In other words, A stands for 'symmetric' and B for 'antisymmetric' to such rotation.

(3) If the molecule has a centre of symmetry, the subscripts g and u are used to label the representations that are respectively symmetric and antisymmetric to inversion.

(4) The subscripts 1 and 2 are used to denote the representations that are symmetric and antisymmetric to reflection in a σ_v-plane.

(5) The superscripts $'$ and $''$ are used respectively to denote the representations that are symmetric and antisymmetric to reflection in a σ_h-plane.

The characters of the irreducible representations of most point groups are integers. However, for certain groups, particularly the C_n groups, complex characters occur and hence for such groups the irreducible representations can be taken in pairs. In other words, the characters of one representation become the complex conjugate of the corresponding characters of the other representation. Such a pair of representations is equivalent to a doubly degenerate representation.

Consider a cyclic group C_n, where each element commutes with every other. It follows, therefore, that each element of a cyclic group is a class by itself. For the C_n group there are n elements, i.e. $C_n, C_n^2, C_n^3, \ldots, C_n^n, = E$, and therefore there are n irreducible representations (see Theorem I in Sec. 9.8). According to Theorem II of Sec. 9.8, i.e.

$$l_1^2 + l_2^2 + \ldots l_n^2 = h$$

each of the n representations will be of dimension one so that each representation is a character. Since the character of the identity operation E must always be one for one-dimensional representation and $C_n^n = E$, we have

$$(\chi_{C_n})^n = \chi_E = 1 \tag{9.40}$$

That is, χ_{C_n} must be equal to the n^{th} root of unity. Such numbers are in general complex and lie on the unit circle in a complex plane and have the form $e^{i\phi}$.

$$(\chi_{C_n})^n = (e^{i\phi})^n = 1 = e^{2\pi mi} \tag{9.41}$$

where m is either zero or any integer. Therefore,

$$n\phi = 2\pi m$$

$$\phi = (2\pi m/n) \tag{9.42}$$

or

$$\chi_{C_n} = e^{(2\pi im/n)} \tag{9.43}$$

The character for C_n will, therefore, be given as

$$\chi^k_{C_n} = e^{(2\pi imk/n)} \tag{9.44}$$

Thus, the characters for the different representations are obtained by setting $m = 0, 1, 2, \ldots$ etc., while the characters for the different elements are obtained by setting $k = 1, 2, 3$, etc.

Let us take, for example, the C_3 group which has the elements C_3, C_3^2 and $C_3^3 = E$. There are three irreducible representations. One representation is obtained by setting $m = 0$, $n = 3$ and $k = 1, 2, 3$ for the three elements, in Eq. (9.44). We then have

$$\begin{array}{ccc} C_3 & C_3^2 & C_3^3 = E \\ 1 & 1 & 1 \end{array}$$

The second representation is obtained by setting $m = 1$, $n = 3$ and $k = 1$, 2, 3 for the three elements. They are

$$\begin{array}{ccc} C_3 & C_3^2 & C_3^3 = E \\ e^{2\pi i/3} & e^{4\pi i/3} & e^{2\pi i} \end{array}$$

The third representation is obtained by setting $m = 2$, $n = 3$ and $k = 1$, 2, 3 for the three elements. They are

$$\begin{array}{ccc} C_3 & C_3^2 & C_3^3 = E \\ e^{4\pi i/3} & e^{8\pi i/3} & e^{4\pi i} \end{array}$$

Since $e^{i\theta} = \cos\theta + i\sin\theta$, one can readily show that

$$e^{2\pi i} = e^{4\pi i} = 1 \tag{9.45}$$

If we use the symbol ϵ for $e^{2\pi i/3}$ then

$$\epsilon = \cos 2\pi/3 + i\sin 2\pi/3 \tag{9.46}$$

One can write

$$e^{4\pi i/3} = \cos\left(2\pi - \frac{2\pi}{3}\right) + i\sin\left(2\pi - \frac{2\pi}{3}\right)$$

$$= \cos 2\pi/3 - i\sin 2\pi/3 = \epsilon^* \tag{9.47}$$

Similarly

$$e^{8\pi i/3} = \cos(2\pi + 2\pi/3) + i\sin(2\pi + 2\pi/3)$$

$$= \cos 2\pi/3 + i\sin 2\pi/3 = \epsilon \qquad (9.48)$$

Using Eqs. (9.45)-(9.48), one can now write down the character table for the C_3 group. It is given in Table 9.4, where two complex conjugate representations Γ_2 and Γ_3 are bracketed together and given the label E.

TABLE 9.4 *The Character Table for the C_3 Group*

		E	C_3	C_3^2
A	$\Gamma 1$	1	1	1
E	$\Gamma 2$	1	ϵ	ϵ^*
	$\Gamma 3$	1	ϵ^*	ϵ

It should be noted that in the C_3 group (in fact, in all C_n groups) the doubly degenerate representation is separable into two one-dimensional representations as shown in Table 9.4.

We shall once again illustrate the above principles in constructing the character table of the point group C_{3v}. This group contains six elements divided into three classes and their multiplication table is recorded as Table 9.2.

Since there are three classes, according to Sec. 9.8, Theorem I, there should be three irreducible representations whose dimensions, l_1, l_2, l_3 satisfy (Sec. 9.8, Theorem II).

$$l_1^2 + l_2^2 + l_3^2 = 6 \qquad (9.49)$$

It is easily seen that the set of integers that satisfy Eq. (9.49) is 1, 1 and 2. We conclude that C_{3v} has two one-dimensional and one two-dimensional irreducible representations.

It should be remembered that the character of any element belonging to one-dimensional representation can be either $+1$ or -1 and the character of the identity operation, E of one-dimension must always be $+1$. For the C_{3v} group there are elements E, C_3, C_3^2, σ_{va}, σ_{vb}, σ_{vc}. According to the multiplication table (9.2), we see that

$$\sigma_{va} \cdot \sigma_{va} = E \qquad (9.50)$$

Hence

$$\chi^2 \sigma_{va} = X_E = 1$$

or

$$\chi\, \sigma_{va} = \pm 1 \qquad (9.51)$$

In other words, the character for any σ_v element of C_{3v} is either $+1$ or -1. The operators C_3 and C_3^2 multiply as

$$C_3 \cdot C_3 = C_3^2 \qquad (9.52)$$

Since C_3^2 belongs to the same class as C_3, we have

$$(\chi_{c_3})^2 = \chi_{c_3} \tag{9.53}$$

or

$$\chi_{c_3}(\chi_{c_3} - 1) = 0$$

i.e.

$$\chi_{c_3} = 1 \text{ or } 0 \tag{9.54}$$

Since the value of χ_{c_3} being zero is ruled out for one-dimensional representation, X_{c_3} must always be $+1$ for all one-dimensional representations. The characters of two one-dimensional representations are therefore obvious and they are shown in Table 9.5.

TABLE 9.5 *The Character Table of* C_{3v}

	E	$2C_3$	$3\sigma_v$
A_1 $\Gamma 1$	1	1	1
A_2 $\Gamma 2$	1	1	-1
E $\Gamma 3$	2	-1	0

The characters of the two-dimensional representation of C_{3v} can be deduced by invoking Eq. (9.35) and from a knowledge of the characters of A_1 and A_2. If we treat the characters $\chi_3(R)$ for the two-dimensional representation as unknown, then from Eq. (9.35) we get

$$\sum_R \chi_1(R)\chi_3(R) = 0$$

i.e.

$$\chi_3(E) + 2\chi_3(C_3) + 3\chi_3(\sigma_v) = 0 \tag{9.55}$$

$$\sum_R \chi_2(R)\chi_3(R) = 0$$

i.e.

$$\chi_3(E) + 2\chi_3(C_3) - 3\chi_3(\sigma_v) = 0 \tag{9.56}$$

From these two equations it is obvious that $\chi_3(\sigma_v) = 0$. Since the identity operator E for any two-dimensional representation must be given by the following matrix

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

its character must be $+2$. Hence from Eq. (9.55) or (9.56) $\chi_3(C_3) = -1$. Thus we have found the set of characters for the two-dimensional representation of C_{3v}. It should be noted that, unlike in the C_3 group, this two-dimensional representation of C_{3v} cannot be separated into two one-dimensional representations.

9.10 Symmetry Properties and Quantum Mechanics

The quantum-mechanical applications of the symmetry properties of molecules are based on the fact that the Schrödinger equation for a molecule is invariant with respect to symmetry operations. Consider the Schrödinger equation

$$H\psi_i = E_i\psi_i \tag{9.57}$$

for some molecular system. Let R be any symmetry operation belonging to the point group of the molecular framework. For example, in H_2O, R could be a reflection in a σ_v-plane which interchanges the hydrogen atoms. An interchange of two hydrogen atoms will not certainly change the potential field acting on the electrons, so that the electronic Hamiltonian of H_2O should remain invariant under such an operation. If H is invariant under the operation R, then H and R commute, so that

$$RH\psi_i = HR\psi_i = E_i(R\psi_i) \tag{9.58}$$

Thus, the function $R\psi_i$ is also an eigenfunction of H with the same eigenvalue E_i. If ψ_i is a non-degenerate eigenfunction then $R\psi_i = K\psi_i$ where K is a constant. In order that $R\psi_i$ be normalised, i.e.

$$K^2\int \psi_i^2\, d\tau = 1$$

$$K = \pm 1 \tag{9.59}$$

If E_i is n-fold degenerate, and suppose $\psi_i^{(1)}, \psi_i^{(2)} \ldots \psi_i^{(n)}$ are the eigenfunctions of H having the common eigenvalue E_i, then

$$H\psi_i^{(1)} = E_i\psi_i^{(1)},\ H\psi_i^{(2)} = E_i\psi_i^{(2)}, \ldots H\psi_i^{(n)} = E_i\psi_i^{(n)} \tag{9.60}$$

Since H is a linear operator, any linear combination of $\psi_i^{(1)}, \psi_i^{(2)}, \ldots \psi_i^{(n)}$ is also a solution of Eq. (9.54) with $E = E_i$, i.e.

$$\begin{aligned} &H\{C_{i1}\psi_i^{(1)} + C_{i2}\psi_i^{(2)} + \ldots C_{in}\psi_i^{(n)}\} \\ &\qquad = E_i[C_{i1}\psi_i^{(1)} + C_{i2}\psi_i^{(2)} + \ldots C_{in}\psi_i^{(n)}] \end{aligned} \tag{9.61}$$

Therefore, the operation of R on any member, say $\psi_i^{(j)}$, of the degenerate set will send it into a linear combination of members of the set, i.e.

$$R\psi_i^{(j)} = \sum_{l=1}^{n} a_{il}\psi_i^{(l)} \tag{9.62}$$

where a_{il}'s must satisfy the boundary condition

$$\sum_{l=1}^{n} a_{il}^2 = 1 \tag{9.63}$$

Similarly, for another operation of S of the group, we also have

$$S\psi_i^{(l)} = \sum_{j=1}^{n} b_{ij}\psi_i^{(j)} \tag{9.64}$$

Thus, the matrices formed from the coefficients in the expansion of $R\psi_i^{(j)}$ and $S\psi_i^{(l)}$, etc., form a representation of the group of operations which leave the Hamiltonian unchanged. The set of eigenfunctions $\psi_i^{(1)}, \psi_i^{(2)}, \ldots \psi_i^{(n)}$ is said to form a basis for a representation of the group, since the representation is generated by the application of operations R, S, etc. Thus, we have established a relation between the wavefunction of a molecule and its symmetry. The wavefunctions which belong to the energy level E_i of a molecule form a function space which gives rise to a representation Γ_i of the point group of the molecule. The question now should be asked whether Γ_i is reducible or irreducible. It is generally assumed that such representation is irreducible. Thus, all possible wavefunctions of a molecule must form bases for some irreducible representations of the point group of the molecule. Since the character tables give information about all possible irreducible representations of the molecular point groups, we can use them to construct the possible wavefunctions of a molecule and their properties.

9.11 Applications

A. (Construction of molecular orbitals of ammonia)

We shall now consider an example from the C_{3v} group and show how the molecular orbitals of NH_3 can be formed. A first step is to take a linear combination of the hydrogen 1*s* atomic orbitals which transform like the irreducible representations of the C_{3v} group. We label the three hydrogen 1*s*-orbitals (Fig. 9.23) as ϕ_a, ϕ_b and ϕ_c which form bases for a new representation. For the identity operator, all three are unchanged and therefore $\chi(E) = 3$. For a C_3 rotation, all three orbitals change their positions, i.e. $\phi_a \rightarrow \phi_b$, $\phi_b \rightarrow \phi_c$ and $\phi_c \rightarrow \phi_a$.

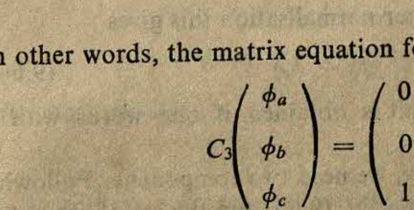


Fig. 9.23 *The hydrogen 1s orbitals in* NH_3 *and the system of axes.*

In other words, the matrix equation for the C_3 rotation is written as

$$C_3\begin{pmatrix}\phi_a\\ \phi_b\\ \phi_c\end{pmatrix} = \begin{pmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 1 & 0 & 0\end{pmatrix}\begin{pmatrix}\phi_a\\ \phi_b\\ \phi_c\end{pmatrix}$$

Hence $\chi(C_3) = 0$. For each reflection there is one function that is unchanged. For example, σ_{va} leaves ϕ_a unchanged but interchanges ϕ_b and ϕ_c (see Fig. 9.12). Hence, the matrix equation for the σ_{va} operation is given by

$$\sigma_{va}\begin{pmatrix}\phi_a\\ \phi_b\\ \phi_c\end{pmatrix} = \begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\phi_a\\ \phi_b\\ \phi_c\end{pmatrix}$$

and $\chi(\sigma_v) = 1$. The character of the new representation Γ is, therefore, given as

	E	$2C_3$	$3\sigma_v$
Γ	3	0	1

We shall now find the component irreducible representations in this representation Γ. For this, we will recall Eq. (9.39) and the Table 9.5. We have

$$a(A_1) = 1/6[3\times1 + 2(0\times1) + 3(1\times1)] = 1$$

$$a(A_2) = 1/6[3\times1 + 2(0\times1) + 3(1\times-1)] = 0$$

$$a(E) = 1/6[3\times2 + 2(0\times-1) + 3(1\times0)] = 1$$

where $a(\Gamma_i)$ is the number of times the irreducible representation Γ_i occurs in the representation Γ above. Thus $\Gamma = A_1 + E$.

The next step is to generate symmetry-adapted functions which transform as A_1 and E. Take one function, say ϕ_a of the basis set and operate on it with each of the operations of the group; multiply the result of each operation by the appropriate character of the irreducible representation and sum the result. That is,

$$\psi_i = \sum_R \chi_i(R)(R\phi) \tag{9.65}$$

where ψ_i is the symmetry-adapted function which transforms like the ith irreducible representation. To illustrate this technique, we operate on ϕ_a with the various operations of the C_{3v} group.

	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
Operating on ϕ_a:	ϕ_a	ϕ_b	ϕ_c	ϕ_a	ϕ_c	ϕ_b

Therefore, from Eq. (9.65) and Table 9.5, we obtain the wavefunction of the A_1 symmetry as

$$\psi(A_1) = \phi_a + \phi_b + \phi_c + \phi_a + \phi_c + \phi_b$$

This is an unnormalised function. After normalisation this gives

$$\psi(A_1) = 1/\sqrt{3}\cdot(\phi_a + \phi_b + \phi_c) \tag{9.66a}$$

It should be noted that the same result is obtained if one works with ϕ_b or ϕ_c.

For the function of the E symmetry, we need two components. Following the same procedure as for A_1, i.e. using Eq. (9.65) and the set of characters for E from Table 9.5, we get

$$\psi_1(E) = 2\phi_a - \phi_b - \phi_c + 0\cdot\phi_a + 0\cdot\phi_c + 0\cdot\phi_b$$

which after normalisation gives

$$\psi_1(E) = 1/\sqrt{6}\cdot(2\phi_a - \phi_b - \phi_c) \tag{9.66b}$$

If we work with ϕ_b, the different operations of C_{3v} on ϕ_b yields

	E	C_3	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
Operating on ϕ_b:	ϕ_b	ϕ_c	ϕ_a	ϕ_c	ψ_b	ϕ_a

using Eq. (9.65) and the characters of E symmetry (Table 9.5) we obtain the following linear combination

$$\psi_2(E) = 1/\sqrt{6}\cdot(2\phi_b - \phi_c - \phi_a) \tag{9.66c}$$

But ψ_1 and ψ_2 are not orthogonal. One method of obtaining orthogonal functions is to follow Schmidt orthogonalisation procedure described in Sec. 2.7.1.

Consider the functions ψ_1 and $\psi_1' = \psi_2 + C\psi_1$ which are orthogonal. Hence

$$\int \psi_1(\psi_2 + C\psi_1)\, d\tau = 0 \tag{9.67}$$

i.e.

$$\int \psi_1\cdot\psi_2\, d\tau + C\int \psi_1^2\, d\tau = 0$$

or

$$C = -\int \psi_1\cdot\psi_2\, d\tau \tag{9.68}$$

Substituting (9.66b) and (9.66c) for ψ_1 and ψ_2 in Eq. (9.68) we obtain

$$\begin{aligned} C &= -1/6\int (-2\phi_a^2 - 2\phi_b^2 + \phi_c^2 + 4\phi_a\phi_b - 2\phi_a\phi_c \\ &\quad + \phi_b\phi_c + \phi_a\phi_b - 2\phi_b\phi_c + \phi_c\phi_a)\, d\tau \\ &= -1/6\left[-2\int \phi_a^2\, d\tau - 2\int \phi_b^2\, d\tau + \int \phi_c^2\, d\tau\right] = +\tfrac{1}{2} \end{aligned} \tag{9.69}$$

where the overlap between two different atomic orbitals is ignored. Hence, the ψ_1' which is orthogonal to ψ_1, is given as

$$\begin{aligned} \psi_1'(E) &= 1/\sqrt{6}\cdot(2\phi_b - \phi_c - \phi_a) + \tfrac{1}{2}\sqrt{1/6}(2\phi_a - \phi_b - \phi_c) \\ &= 1/\sqrt{6}\cdot(2\phi_b - \tfrac{1}{2}\phi_b - \phi_c - \tfrac{1}{2}\phi_c - \phi_a + \phi_a) \\ &= 1/\sqrt{6}\cdot(3/2\phi_b - 3/2\phi_c) \end{aligned}$$

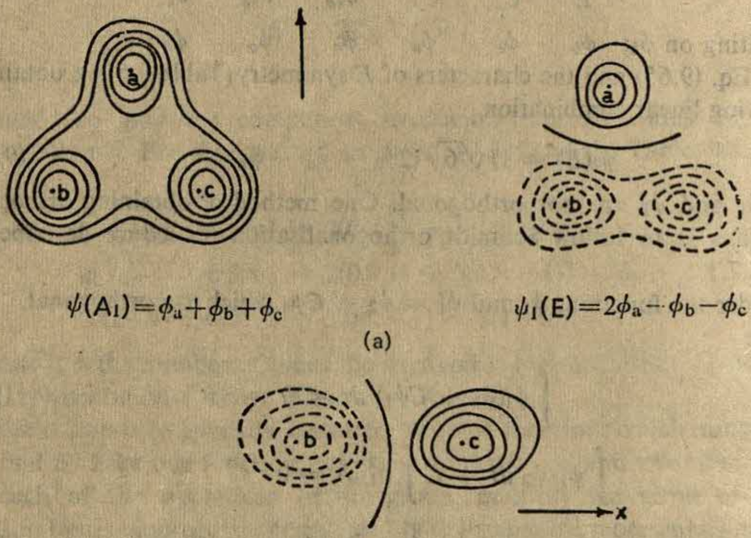
After normalisation

$$\psi_1'(E) = 1/\sqrt{2}\cdot(\phi_b - \phi_c) \tag{9.70}$$

We have thus obtained the following symmetry orbitals of the A_1 and E symmetries.

$$\begin{aligned} \psi(A_1) &= 1/\sqrt{3}\cdot(\phi_a + \phi_b + \phi_c) \\ \psi_1(E) &= 1/\sqrt{6}\cdot(2\phi_a - \phi_b - \phi_c) \\ \psi_1'(E) &= 1/\sqrt{2}\cdot(\phi_b - \phi_c) \end{aligned} \tag{9.71}$$

and the schematic diagrams of the contours of these orbitals are shown in Fig. 9.24.



$\psi(A_1)=\phi_a+\phi_b+\phi_c$ $\psi_1(E)=2\phi_a-\phi_b-\phi_c$

(a)

$\psi_1'(E)=\phi_b-\phi_c$

Fig. 9.24 *The schematic diagram of the contours of the orbitals* $\psi(A_1)$, $\psi_1(E)$ *and* $\psi_1'(E)$ *of Eq. (9.71).*

Turning to NH$_3$, the above three ligand orbitals given by Eq. (9.71) must be combined with the four valence orbitals of the N atom, i.e. $2s$, $2p_x$, $2p_y$ and $2p_z$. The $2s$ and $2p_z$ orbitals transform like the totally symmetric representation A_1 as shown below:

$$E(2s)=(2s),\qquad C_3(2s)=2s,\qquad \sigma_v(2s)=2s$$

$$E(2p_z)=2p_z,\qquad C_3(2p_z)=2p_z,\qquad \sigma_v(2p_z)=2p_z$$

Since the p_x and p_y orbitals behave in the same way as x and y, we consider the rotation of the x- and y-axes by an arbitrary angle θ to x' and y' (Fig. 9.25).

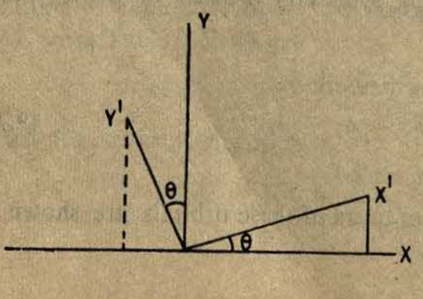


Fig. 9.25 *The rotation of x- and y-axes by an angle* θ *in the x–y plane.*

Then, $$x' = x\cos\theta + y\sin\theta$$

$$y' = -x\cos(90^\circ - \theta) + y\sin(90^\circ - \theta)$$

$$= -x\sin\theta + y\cos\theta$$

i.e. $$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

Therefore an operation of rotation on p_x or p_y gives a mixture of p_x and p_y hence the $2p_x$ and $2p_y$ orbitals must belong to the doubly degenerate representation. Thus $X(C_3) = 2\cos 120^\circ = -1$. A σ_v-operation, say $\sigma_v(xz)$ on p_x and p_y gives the matrix

$$\sigma_v(xz)\begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} p_x \\ p_y \end{pmatrix} \quad \text{hence } X(\sigma_v) = 0$$

Thus, we have the following set of characters for $2p_x$ and $2p_y$ orbitals

$$\begin{array}{ccc} E & 2C_3 & 3\sigma_v \\ 2 & 1 & 0 \end{array}$$

Therefore, the $2p_x$, and $2p_y$ orbitals transform like the E-representation of the C_{3v} group.

When combining the ligand orbitals with the valence orbitals of the N-atom, it should be noted that they must belong to the same symmetry. One obtains, thus, bases for the linear combination as given in Table 9.6. The choice of axes is shown in Fig. 9.23. Figure 9.24 shows that $\psi_1(E)$ and $\psi_1'(E)$ must combine respectively with $2p_y$ and $2p_x$ orbitals.

TABLE 9.6 *Bases of Irreducible Representations of C_{3v}*

Symmetry	*Ligand orbitals*	*Central atom orbitals*
A_1	$1/\sqrt{3}\cdot(\phi_a+\phi_b+\phi_c)$	$2s, 2p_z$
E	$\left\{\begin{array}{l} 1/\sqrt{2}\cdot(\phi_b - \phi_c) \\ 1/\sqrt{6}\cdot(2\phi_a - \phi_b - \phi_c) \end{array}\right.$	$2p_x$ $2p_y$

It follows therefore from Table 9.6 that the M.O. of the A_1 symmetry for NH_3 has the form

$$\phi_1 = C_1\cdot 1/\sqrt{3}\cdot(\phi_a + \phi_b + \phi_c) + C_2\cdot 2s + C_3\cdot 2p_z \qquad (9.72)$$

where the coefficients C_i could be determined from a 3×3 determinant. Similarly, the MOs of the E symmetry have the forms

$$\phi_2 = C_1' 1/\sqrt{2}\cdot(\phi_b - \phi_c) + C_2' 2p_x$$

$$\phi_2 = C_1'' 1/\sqrt{6}\cdot(2\phi_a - \phi_b - \phi_c) + C_2'' 2p_y$$

The coefficients C_i' and C_i'' can be determined from the two 2×2 determinants.

B. Use of symmetry in Huckel theory of organic molecules

Simple Huckel calculations for π-electrons in large conjugated systems call for solution of $n\times n$ determinant. When n is large the work involved becomes prohibitive unless a digital computer is employed. However, the work can be appreciably reduced whenever the molecule has a symmetry in which case the $n\times n$ determinant may be replaced by two or more smaller determinants.

We shall consider naphthalene as an example. This molecule belongs to the D_{2h} symmetry. If we disregard the horizontal plane of symmetry for the sake of a simplicity, we can assign the molecule to the C_{2v} type. Since we deal with the π-electrons only, we are concerned with the $2p_\pi$ atomic orbitals, ϕ's, of the ten carbon atoms which form bases for a new representation. The labelling of atoms and the axes are shown in Fig. 9.26, and the character table of the C_{2v} group is given in Table 9.7. The set of characters for the new representation Γ is shown at the bottom row of Table 9.7. This representation can be reduced to the component irreducible representations of C_{2v} following the same procedure as in the case of ammonia. We get from Eq. (9.39) and Table 9.7.

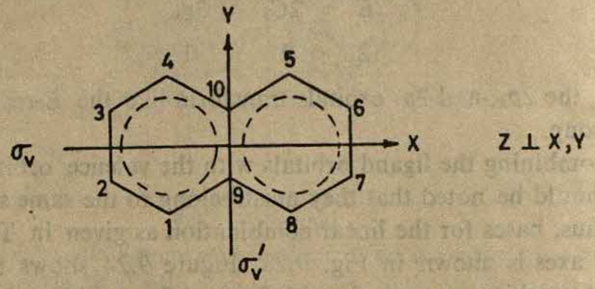


Fig. 9.26 *A naphthalene molecule and its axes.*

TABLE 9.7 *Character Table of the C_{2v} Group*

	E	$C_2(z)$	σv	$\sigma v'$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1
Γ	10	0	0	2

$$a(A_1) = \frac{1}{4}\,(10\times 1 + 0\times 1 + 0\times 1 + 2\times 1] = 3$$

$$a(A_2) = \frac{1}{4}\,[10\times 1 + 0\times 1 + 0\times -1 + 2\times -1] = 2$$

$$a(B_1) = \frac{1}{4}\,[10\times 1 + 0\times -1 + 0\times 1 + 2\times -1] = 2$$

$$a(B_2) = \frac{1}{4}\,[10\times 1 + 0\times -1 + 0\times -1 + 2\times 1] = 3$$

where a (Γ_i) is the number of times the i^{th} irreducible representation occurs in Γ above. Thus, we have

$$\Gamma = 3A_1 + 2A_2 + 2B_1 + 3B_2$$

The next step is to generate symmetry-adapted functions of the A_1, A_2, B_1 and B_2 symmetries. To illustrate this, we operate on the atomic orbitals ϕ_1, ϕ_2, etc., which are localised on atoms 1, 2, etc., respectively (Fig. 9.26), with the various operations of C_{2v}. The result is as follows. Applying Eq. (9.65) and using the set of characters for A_1 from Table 9.7, we obtain the following set of the normalised functions of the A_1 symmetry.

	E	$C_2(z)$	σv	$\sigma v'$
Operating on ϕ_1	ϕ_1	ϕ_5	ϕ_4	ϕ_8
Operating on ϕ_2	ϕ_2	ϕ_6	ϕ_3	ϕ_7
Operating on ϕ_3	ϕ_3	ϕ_7	ϕ_2	ϕ_6
Operating on ϕ_4	ϕ_4	ϕ_8	ϕ_1	ϕ_5
Operating on ϕ_5	ϕ_5	ϕ_1	ϕ_8	ϕ_4
Operating on ϕ_6	ϕ_6	ϕ_2	ϕ_7	ϕ_3
Operating on ϕ_7	ϕ_7	ϕ_4	ϕ_6	ϕ_2
Operating on ϕ_8	ϕ_8	ϕ_4	ϕ_5	ϕ_1
Operating on ϕ_9	ϕ_9	ϕ_{10}	ϕ_{10}	ϕ_9
Operating on ϕ_{10}	ϕ_{10}	ϕ_9	ϕ_9	ϕ_{10}

$$\begin{aligned}
\psi_1 &= 1/\sqrt{4}\cdot(\phi_1 + \phi_4 + \phi_5 + \phi_8)\\
\psi_2 &= 1/\sqrt{4}\cdot(\phi_2 + \phi_3 + \phi_6 + \phi_7) \qquad (9.74)\\
\psi_3 &= 1/\sqrt{2}\cdot(\phi_9 + \phi_{10})
\end{aligned}$$

The other combinations are merely the duplicates of these three functions.

Following similar procedure for the A_2, B_1 and B_2 symmetries, we obtain the following results:

$$A_2\begin{cases}\psi_3 = 1/\sqrt{4}\cdot(\phi_1 + \phi_5 - \phi_4 - \phi_8)\\ \psi_4 = 1/\sqrt{4}\cdot(\phi_2 + \phi_6 - \phi_3 - \phi_7)\end{cases} \qquad (9.75)$$

$$B_1\begin{cases}\psi_5 = 1/\sqrt{4}\cdot(\phi_1 - \phi_5 + \phi_4 - \phi_8)\\ \psi_6 = 1/\sqrt{4}\cdot(\phi_2 - \phi_6 + \phi_3 - \phi_7)\end{cases} \qquad (9.76)$$

$$B_2\begin{cases}\phi_7 = 1/\sqrt{4}\cdot(\phi_1 - \phi_5 - \phi_4 + \phi_8)\\ \phi_8 = 1/\sqrt{4}\cdot(\phi_2 - \phi_6 - \phi_3 + \phi_7)\\ \phi_9 = 1/\sqrt{2}\cdot(\phi_9 - \phi_{10})\end{cases} \qquad (9.77)$$

Thus, we see that instead of solving a 10 × 10 determinant for the energy levels and the molecular orbitals of naphthalene, we need to solve two 3×3- and two 2×2- determinants.

We shall now set up the determinant for the A_1 symmetry. Following the Huckel approximations described in Sec. 8.3, we have

$$\begin{aligned}
\langle \psi_1 | H | \psi_1 \rangle &= \tfrac{1}{4}[\langle \phi_1 | H | \phi_1 \rangle + \langle \phi_4 | H | \phi_4 \rangle \\
&\quad + \langle \phi_5 | H | \phi_5 \rangle + \langle \phi_8 | H | \phi_8 \rangle] \\
&= \alpha \\
\langle \psi_2 | H | \psi_2 \rangle &= \tfrac{1}{4}[\langle \phi_2 | H | \phi_2 \rangle + \langle \phi_3 | H | \phi_3 \rangle \\
&\quad + \langle \phi_6 | H | \phi_6 \rangle + \langle \phi_7 | H | \phi_7 \rangle \\
&\quad + 2\langle \phi_2 | H | \phi_3 \rangle + 2\langle \phi_6 | H | \phi_7 \rangle] \\
&= \alpha + \beta \\
\langle \psi_3 | H | \psi_3 \rangle &= \tfrac{1}{2}[\langle \phi_9 | H | \phi_9 \rangle + \langle \phi_{10} | H | \phi_{10} \rangle \\
&\quad + 2\langle \phi_9 | H | \phi_{10} \rangle] \\
&= \alpha + \beta \\
\langle \psi_1 | H | \psi_2 \rangle &= \tfrac{1}{4}[2\langle \phi_1 | H | \phi_2 \rangle + 2\langle \phi_5 | H | \phi_6 \rangle \\
&\quad + 2\langle \phi_3 | H | \phi_4 \rangle + 2\langle \phi_7 | H | \phi_8 \rangle] \\
&= 2\beta \\
\langle \psi_1 | H | \psi_3 \rangle &= 1/\sqrt{4}.1/\sqrt{2}\,[2\langle \phi_1 | H | \phi_9 \rangle \\
&\quad + 2\langle \phi_8 | H | \phi_9 \rangle + 2\langle \phi_4 | H | \phi_{10} \rangle \\
&\quad + 2\langle \phi_5 | H | \phi_{10} \rangle] \\
&= 2\sqrt{2}\cdot\beta \\
\langle \psi_2 | H | \psi_3 \rangle &= 0
\end{aligned}$$

Setting $X = (\alpha - E)/\beta$

The 3×3 determinant is given as

$$\begin{vmatrix} X & 2 & 2\sqrt{2} \\ 2 & X+1 & 0 \\ 2\sqrt{2} & 0 & X+1 \end{vmatrix} = 0 \tag{9.78}$$

Similarly, the determinants for the other symmetry species can be set up and solved for the energy level and the molecular orbitals of naphthalene, following the same procedure as described in Sec. 8.4.

C. *The direct product and its importance*

Consider any doubly degenerate function f' which can be expressed as a linear combination of the two component functions f_1 and f_2, as

$$f' = a_{11}f_1 + a_{12}f_2$$

Similarly, another doubly degenerate function, g can be written as

$$g' = b_{11}g_1 + b_{12}g_2$$

Multiplication of f' and g' gives

$$\begin{aligned}
f'g' &= a_{11}f_1 \times b_{11}g_1 + a_{11}f_1 \times b_{12}g_2 \\
&\quad + a_{12}f_2 \times b_{11}g_1 + a_{12}f_2 \times b_{12}g_2
\end{aligned}$$

which is a linear combination of four product functions. Consequently, it is to be expected that the transformation matrix of the product $f' \times g'$ is a 4×4 matrix. Such a matrix is the direct product of the two 2×2 matrices, formed by the rule:

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \times \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}$$

$$= \begin{bmatrix} a_{11}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} & a_{12}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \\ a_{21}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} & a_{22}\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \end{bmatrix}$$

$$= \begin{bmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{bmatrix}$$

The character of the direct product is obviously

$$a_{11}b_{11} + a_{11}b_{22} + a_{22}b_{11} + a_{22}b_{22} = (a_{11} + a_{22})\,(b_{11} + b_{22}),$$

i.e. the product of the characters of the two individual matrices. A similar method can be applied to species of higher degeneracy. Thus, if a and b are two matrices and c is the direct product of a and b then

$$\chi(c) = \chi(a)\,\chi(b) \tag{9.79}$$

The representation of the direct product of two irreducible representations is, in general, a reducible representation but this can be decomposed into the irreducible components according to the method given earlier. For example, the direct product $E \times E$ of the C_{3v} group (Table 9.5) has the following set of characters

	E	$2C_3$	$3\sigma_v$
$E \times E$	4	1	0

From Eq. (9.39) and Table 9.5, we have

$$a(A_1) = 1/6\,[4 \times 1 + 2\,(1 \times 1) + 3\,(0 \times 1)] = 1$$

$$a(A_2) = 1/6\,[4 \times 1 + 2\,(1 \times 1) + 3\,(0 \times -1)] = 1$$

$$a(E) = 1/6\,[4 \times 2 + 2\,(1 \times -\ 1) + 3\,(0 \times 0)] = 1$$

Thus

$$E \times E = A_1 + A_2 + E$$

The usefulness of the concept of the direct product appears when integrals of the type $\int \psi_i \cdot \hat{O} \cdot \psi_j \, d\tau$ have to be evaluated where $\hat{O}$ is an operator. Such an integrand is different from zero if it is invariant under all the operations of the group. If the integrand changes sign under a symmetry operation, it will have a value in one part of space equal and opposite to that in an equivalent portion of space. The integral over all space would then be zero. Therefore, for the nonzero value of the integral, the direct product of the representations $\Gamma(\psi_i)$ and $\Gamma(\psi_j)$ must contain an irreducible component having the same properties as the operator $\hat{O}$, i.e.

$$\Gamma(\psi_i)\times\Gamma(\psi_j) = \Gamma(O) \tag{9.80}$$

Since the Hamiltonian is totally symmetric and therefore invariant under any operation of group, the integral $\int \psi_i \mid H \mid \psi_j \, d\tau$ is different from zero only if $\Gamma(\psi_i) = \Gamma(\psi_j)$, because, the product of two anti-symmetric or two symmetric functions is symmetric just as $-1\times-1 = +1$ and $+1\times+1 = +1$. Or the direct product given by

$$\Gamma(\psi_i)\times\Gamma(\psi_j) = \sum_i a_i\Gamma_i \tag{9.81}$$

is such that at least one component Γ_i on the right hand side of Eq. (9.81) is totally symmetric.

The most interesting application of the concept of the direct product in the context of symmetry is the determination of selection rules in the electronic and vibrational spectroscopy. Application of these rules specifies whether a given transition between two states is allowed or forbidden. The probability of a transition is proportional to the square of the transition moment, which is defined as,

$$\vec{\mu} = \int \psi_i \hat{M}\cdot\psi_f \, dr \tag{9.82}$$

where ψ_i and ψ_f are the initial and final state wavefunctions and $\vec{M}$, a dipole moment vector with components $M_x = \Sigma\, e_j x_j$; $M_y = \Sigma\, e_j y_j$ and $M_z = \Sigma\, e_j z_j$, where e_j is the charge of the j^{th} particle having coordinate x_j, y_j and z_j and the summation extends over all nuclei and electrons. The wavefunctions ψ_i, ψ_j are functions of the coordinates of all these particles and the integration extends over all space in all these particles.

We shall consider the case of formaldehyde H_2CO which belongs to C_{2v} and examine how the selection rules for its various electronic transitions can be derived from the symmetry considerations. The system of axes for the CH_2O molecule is shown in Fig. 9.27.

The various operations of C_{2v} on the x, y and z axes give us the matrix equations

$$E\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

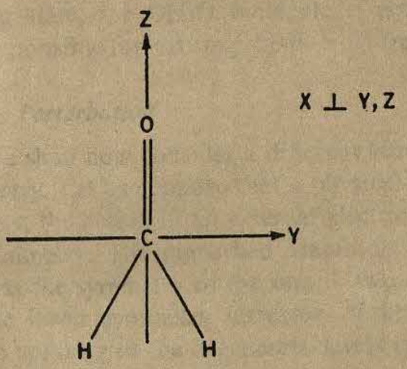


Fig. 9.27 *The system of axes for the formaldehyde molecule.*

$$C_2(z)\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\sigma_v(xz)\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\sigma_v'(yz)\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

This shows that x belongs to B_1, y to B_2 and z to A_1 representations. The orbitals $2p_x$, $2p_y$ and $2p_z$ transform as x, y and z while the 2s-orbitals, being spherical, should transform as A_1. The ten valence atomic orbitals in CH_2O which form bases for the linear combination are distributed among the symmetry classes of C_{2v}, in accordance with the scheme given in Table 9.8.

TABLE 9.8 *Symmetry Distribution of Ten Valence Orbitals in Formaldehyde*

Symmetry species	*Carbon orbitals*	*Oxygen orbitals*	*Hydrogen orbitals*
A_1	2s, 2pz	2s, 2pz	Ha(1s) + Hb(1s)
A_2	—	—	—
B_1	2px	2px	—
B_2	2py	2py	Ha(1s) − Hb(1s)

The symmetry of the σ and σ^* orbitals corresponding to the C–O bond in CH_2O is A_1, that of π and π^* orbitals is B_1 while the lone pair orbital, n, on oxygen is $2p_x$ which has the symmetry B_2. The energy level diagram for orbitals of the carbonyl group is shown in Fig. 9.28.

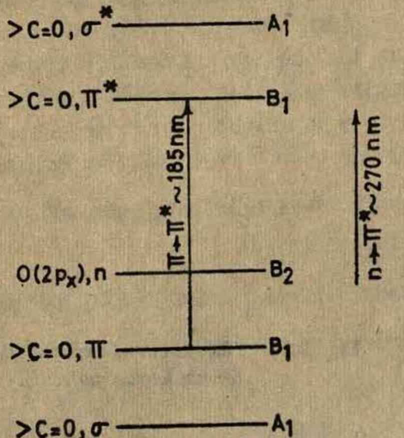


Fig. 9.28 *The energy level diagram for the various orbitals of a carbonyl group.*

The completely filled orbitals are always symmetric with respect to any symmetry operation and to find out the overall electronic symmetry of an excited state we consider only the orbitals that have unpaired electron. The lowest electronic energy transition in CH_2O is from n to π^*. Hence in the n–π^* state of CH_2O, the n and π^* orbitals each have one unpaired electron. The overall symmetry of the $n\pi^*$ state is $B_2 \times B_1 = A_2$. The ground state containing each orbital with paired electrons is totally symmetric, i.e. A_1. Therefore, the transition moment for the $n \rightarrow \pi^*$ transition in CH_2O is given by

$$\int A_1 \cdot \hat{M} \cdot A_2 d\tau = A_1 \times A_2 \times \Gamma(\hat{M}) = A_2 \times \Gamma(\hat{M}) \tag{9.83}$$

Since the components of the dipole moment vector $\hat{M}$, i.e. M_x, M_y and M_z transform in the same way as x, y and z and since none of these components has the symmetry A_2, the integral of Eq. (9.83) is zero. Such a transition is therefore forbidden. The second transition is from $\pi \rightarrow \pi^*$ and the overall symmetry of the $\pi\pi^*$ state is $B_1 \times B_1 = A_1$. Since the z component of $\bar{M}$ has the symmetry A_1, the transition moment integral, i.e. $\int A_1 \bar{M} A_1 \, d\tau$ is non-zero and the transition is allowed. Formaldehyde vapour has a strong absorption at 185 nm which is due to $\pi \rightarrow \pi^*$ transition.

The above symmetry considerations do not tell us how intense the absorption will be. They merely tell us whether or not there is any symmetry prohibition on its taking place. The $n \rightarrow \pi^*$ transition in CH_2O is forbidden on the ground of symmetry but a weak band is observed at 270 nm. Why does such a transition occur even weakly? It should be remembered that the above symmetry arguments are only rigorous if the molecule had the perfect C_{2v} symmetry in both the ground and excited states. In the ground state certain unsymmetrical vibrations can distort the molecule and reduce its symmetry. In the excited state it has been shown that even in the nonvibrating state, the CH_2O molecule is not quite planar. Both these effects are responsible for making the $n \rightarrow \pi^*$ transition weakly allowed.

D. Perturbation

We shall now consider a different kind of application of the theory of symmetry. Let us suppose that a physical system is subjected to a perturbation (say, the action of an external electric field). The external field has a certain symmetry. The perturbed Hamiltonian is $H = H_0 + V$. It is to be noted that the symmetry of the sum of two operators is always the symmetry of the lower symmetry operator. If the symmetry of H is same as that of H_0, no splitting of the degenerate levels occurs. If, however, the symmetry of the perturbation V is lower than that of H_0 then the symmetry of H is same as that of V. The wavefunctions of H_0, which belonged to some irreducible representations, will now form the representations of the symmetry group of the perturbed H, but these representations may be reducible due to lowering of the symmetry. This means that the degenerate levels are split.

An important example is the splitting of the five *d*-levels in a crystal field of the O_h symmetry. The unperturbed H_0 relates to a free atom and it has the complete spherical symmetry. If this atom is placed in an electric field of the O_h symmetry, then from the character table of O_h (see Appendix 9), the d_{z2} and $d_{x^2-y^2}$ orbitals transform according to the E_g representation while d_{xy}, d_{yz} and d_{xz} transform according to the T_{2g} representation. The d_{z2} and $d_{x^2-y^2}$ orbitals point along the axes while d_{xy}, d_{yz} and d_{zx} are directed between the axes. If the field of ligands is due to point negative charges, then an electron in the d_{xy}, d_{yz} and d_{xz} orbitals will have a lower energy than one in d_{z^2} and $d_{x^2-y^2}$. The five previously degenerate *d*-orbitals of an atom are now split in an O_h symmetry, as shown in Fig. 9.29.

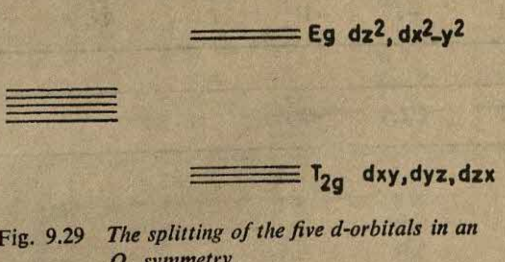


Fig. 9.29 *The splitting of the five d-orbitals in an O_h symmetry.*

The crystal field transition from $T_{2g} \rightarrow E_g$ can now occur if the five *d*-orbitals are not completely filled. This is a very common phenomenon among the hexa-coordinated transition metal complexes. On the other hand, the three *p*-orbitals, p_x, p_y and p_z are still degenerate and belong to T_{1u} in the octahedral complex, because they have exactly equivalent positions with respect to ligands. Hence the crystal field transition involving *p*-orbitals in a complex of the O_h symmetry cannot be observed.

APPENDIX 9

This appendix lists the character tables of a few important point groups that are commonly encountered in real molecules. The procedure for the construction of the character tables and the nomenclature for the various symmetry species are discussed in Sec. 9.9. The first column of each table lists the various symmetry species, the body of the table lists the set of characters for each symmetry species, the last but one column lists the three coordinate axes x, y, z and the three rotations, R_x, R_y and R_z and the last column gives the product of the coordinates such as xy, x^2, yz, etc.

C_2	E	$C_2(z)$		
A	1	+1	z, Rz	x^2, y^2, z^2, xy
B	1	−1	$x, y, Rx, Ry,$	

C_3	E	$C_3(z)$	C_3^2		
A	1	+1	+1	z, Rz	$X^2 + y^2, z^2$
E	1	ϵ	ϵ^*	x, y	xy, yz
	1	ϵ^*	ϵ	(Rx, Ry)	x^2-y^2, xy

C_4	E	$C_4(z)$	C_2	C_4^3		
A	1	+1	+1	+1	z, Rz	x^2+y^2, z^2
B	1	−1	+1	−1	—	x^2-y^2, xy
E	1	i	−1	$-i$	x, y	
	1	$-i$	−1	i	Rx, Ry	(xz, yz)

C_{2v}	E	$C_2(z)$	$\sigma v(xz)$	$\sigma v'(yz)$		
A_1	1	+1	+1	+1	z	x^2, y^2, z^2
A_2	1	+1	−1	−1	Rz	xy
B_1	1	−1	+1	−1	x, Ry	xz
B_2	1	−1	−1	+1	y, Rx	yz

C_{3v}	E	$2C_3$	$3\sigma v$		
A_1	1	+1	+1	z	$x^2+y^2+z^2$
A_2	1	+1	−1	Rz	—
E	2	−1	0	x, y	(x^2-y^2, xy)
				Rx, Ry	(xy, yz)

C_{4v}	E	C_2	$2C_4(z)$	$2\sigma v$	$2\sigma d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	Rz	—
B_1	1	1	-1	1	-1	—	x^2-y^2
B_2	1	1	-1	-1	1	—	xy
E	2	-2	0	0	0	$x, y,$ Rx, Ry	xz, yz

C_2h	E	C_2^z	$\sigma h(xy)$	i		
Ag	1	1	1	1	Rz	x^2, y^2, z^2, xy
Au	1	1	-1	-1	z	—
Bg	1	-1	-1	-1	Rx, Ry	xz, yz
Bu	1	-1	$+1$	-1	x, y	—

$$C_3h = C_3 \times \sigma h$$

S_2	E	i		
Ag	1	1	Rx, Ry, Rz	$x^2, y^2, z^2, xy, yz, xz$
Au	1	-1	x, y, z	

S_4	E	C_2	S_4	S_4^3		
A	1	1	1	1	Rz	x^2+y^2, z^2
B	1	1	-1	-1	z	
E	1	-1	i	$-i$	x, y	xz, yz
	1	-1	$-i$	i	Rx, Ry	x^2-y^2, xy

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A_1	1	1	1	1	—	x^2, y^2, z^2
B_1	1	1	-1	-1	z, Rz	xy
B_2	1	-1	1	-1	y, Ry	xz
B_3	1	-1	-1	1	x, Rx	yz

D_3	E	$2C_3$	$3C_2'$		
A_1	1	1	1	—	x^2+y^2, z^2
A_2	1	1	-1	R_z, z	—
E	2	-1	0	(x, y)	xz, yz
				(Rx, Ry)	x^2-y^2, xy

D_4	E	C_2	$2C_4(z)$	$2C_2$	$2C_2''$		
A_1	1	1	1	1	1	—	x^2+y^2, z^2
A_2	1	1	1	−1	−1	z, R_z	—
B_1	1	1	−1	1	−1	—	—
B_2	1	1	−1	1	1	—	—
E	2	−2	0	0	0	x, y Rx, Ry	xz, yz x^2-y^2, xy

D_2h	E	C_2z	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
Ag	1	1	1	1	1	1	1	1	—	x^2, y^2, z^2
Au	1	1	1	1	−1	−1	−1	−1	—	—
B_1g	1	1	−1	−1	+1	+1	−1	−1	R_z	xy
B_1u	1	1	−1	−1	−1	−1	+1	+1	z	—
B_2g	1	−1	+1	−1	+1	−1	+1	−1	Ry	xz
B_2u	1	−1	+1	−1	−1	+1	−1	+1	y	—
B_2g	1	−1	−1	+1	+1	−1	−1	+1	Rx	yz
B_3u	1	−1	−1	+1	−1	+1	+1	−1	x	—

D_3h	E	$\sigma_h(xy)$	$2C_3(z)$	$2S_3$	$3C_2$	$3\sigma_v$		
A_1'	1	1	1	1	1	1	—	x^2+y^2, z^2
A_2'	1	1	1	1	−1	−1	R_z	—
A_2''	1	−1	1	−1	1	−1	—	—
E'	2	2	−1	−1	0	0	(x, y)	x^2-y^2, xy
E''	2	−2	−1	1	0	0	Rx, Ry	xy, yz

D_4h	E	$2C_4(z)$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma v$	$2\sigma d$		
A_1g	1	1	1	1	1	1	1	1	1	1	—	x^2+y^2, y^2
A_1u	1	1	1	1	1	−1	−1	−1	−1	−1	—	—
A_2g	1	1	1	−1	−1	1	1	1	−1	−1	Rz	—
A_2u	1	1	1	−1	−1	−1	−1	−1	1	1		
B_1g	1	−1	1	1	−1	1	−1	1	1	−1	—	x^2-y^2
B_1u	1	−1	1	1	−1	−1	1	−1	−1	1	—	—
B_2g	1	−1	1	−1	1	1	−1	1	−1	1	—	xy
B_2u	1	−1	1	−1	1	−1	1	−1	1	−1	—	—
Eg	2	0	−2	0	0	2	0	−2	0	0	Rx, Ry	xz, yz
Eu	2	0	−2	0	0	−2	0	2	0	0	x, y	—

D_6h	E	$2C_6(z)$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	$\sigma_h(xy)$	$3\sigma_d$	$3\sigma v$		
A_1g	1	1	1	1	1	1	1	1	1	1	1	1	—	x^2+y^2, z^2
A_1u	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	—	—
A_2g	1	1	1	1	−1	−1	1	1	1	1	−1	−1	Rz	—
A_2u	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	—
B_1g	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	—	—
B_1u	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	—	—
B_2g	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1	—	—
B_2u	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1	—	—
E_1g	2	1	−1	−2	0	0	2	1	−1	−2	0	0	Rx, Ry	yz, xz
E_1u	2	1	−1	−2	0	0	−2	−1	1	2	0	0	x, y	
E_2g	2	−1	−1	2	0	0	2	−1	−1	2	0	0	—	$x^2-y^2,(xy)$
E_2u	2	−1	−1	2	0	0	−2	1	1	−2	0	0	—	—

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma d$		
A_1	1	1	1	1	1	—	$x^2+y^2+z^2$
A_2	1	1	1	−1	−1	—	—
E	2	−1	2	0	0	—	$3z^2-r^2, x^2-y^2$
T_1	3	0	−1	1	−1	Rx, Ry, Rz	—
T_2	3	0	−1	−1	1	x, y, z	xy, yz, zx

Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma d$		
A_1g	1	1	1	1	1	1	1	1	1	1	—	$x^2+y^2+z^2$
A_2g	1	1	−1	−1	1	1	−1	1	1	−1	—	—
A_1u	1	1	1	1	1	−1	−1	−1	−1	−1	—	—
A_2u	1	1	−1	−1	1	−1	1	−1	−1	1	—	—
Eg	2	−1	0	0	2	2	0	−1	2	0	—	$3z^2-r^2$, x^2-y^2
Eu	2	−1	0	0	2	−2	0	1	−2	0	—	—
T_1g	3	0	−1	1	−1	3	1	0	−1	−1	Rx, Ry, Rz	
T_2g	3	0	1	−1	−1	3	−1	0	−1	1	—	xy, yz, zx
T_1u	3	0	−1	1	−1	−3	−1	0	1	1	x, y, z	—
T_2u	3	0	1	−1	−1	−3	1	0	1	−1	—	—

	$C^* \infty v$	E	$2C\varphi$	σv		
Σ^+	A_1	1	1	1	—	x^2+y^2, z^2
Σ^-	A_2	1	1	−1	z, Rz	—
π	E_1	2	$2\cos\varphi$	0	x, y, Rx, Ry	xz, yz
Δ	E_2	2	$2\cos 2\varphi$	0	—	x^2-y^2, xy
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.

$D^*\infty h$		E	$2C\varphi$	C_2'	i	$2iC\varphi$	iC_2'		
Σ_g^+	A_1g	1	1	1	1	1	1	–	$x^1+y^2+z^2$
Σ_u^+	A_1u	1	1	1	-1	-1	-1	–	–
Σ_g^-	A_2g	1	1	1	1	1	-1	Rz	–
Σ_u^-	A_2u	1	1	-1	-1	-1	1	z	–
πg	E_1g	2	$2\cos\varphi$	0	2	$2\cos\varphi$	0	Rx, Ry	yz, xz
πu	E_1u	2	$2\cos\varphi$	0	-2	$-2\cos\varphi$	0	x, y	–
Δg	E_2g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0	–	x^2-y^2, xy
Δu	E_2u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0	–	–

*The first column for the $C\infty v$ and $D\infty h$ groups gives the spectroscopic symbols corresponding to the symmetry symbols. The meaning of the spectroscopic symbols is discussed in Sec. 7.8.

PROBLEMS

1. What are the point groups of the following molecules or ions?
   ICl_4^-, C_2H_4, C_4H_8 (cyclobutane), C_5H_5N (pyridine),
   1 : 3 : 5 trichlorobenzene, CO_2, CCl_4.
2. BrF_5 belongs to the C_{4v} group. Find the multiplication table for C_{4v}. Divide the elements into the possible different classes. Find the number of one- and two-dimensional irreducible representations of C_{4v}.
3. Find from the character table the direct product $E_{1u} \times E_{1u}$ in the D_{6h} group. Show that its irreducible components are A_{1g}, A_{2g} and E_{2g}.
4. The methyl radical is planar and has the D_{2h} symmetry. Give a qualitative account of the molecular orbitals of this radical from the symmetry arguments and identify the symmetry of the orbital that has the unpaired electron.
5. $Ni(CN)_4^=$ has the D_4h symmetry. Find how the five d-orbitals of the metal atom transform in the D_4h symmetry.
6. Classify the three π-molecular orbitals of the allyl system (Sec. 8.4) according to the irreducible representations of C_{2v}.
7. Methane has the Td symmetry. Find from the character table the possible linear combinations of the hydrogen $1s$ orbitals that transform like the irreducible representations of the Td group.

10

Semi-empirical and Ab Initio SCF Theories

10.1 Introduction

In Chapter 8 we discussed the self-consistent field formulation of the simple molecular orbital theory based on the many-electron hamiltonian according to Roothaan's procedure. So far as the π-electrons are concerned this theory is quite successful. But in saturated molecules or in general, any polyatomic molecule it is usually necessary to invoke several valence atomic orbitals on each atom and the situation becomes somewhat more complicated. However, various approximations are now known to make the problem look less complicated even for fairly large molecules. Some of these theories go beyond simple Hückel-type MO theory in so far as they are based on a full quantum-mechanical treatment of the many-electron systems and explicitly include electron interactions. There are basically two approaches now known as (1) semiempirical MO theories, (2) ab initio-MO theories. Both these theories are based on Roothaan's self consistent field procedure. In semiempirical theories many approximations are made in order to achieve maximum simplicity by appeal to various experimental data on atoms and molecules. In ab initio theories, the various integrals required to set up the secular equations are calculated explicitly and after carrying through the SCF procedure the molecular orbitals are derived. Obviously, for a given size of computation, the semiempirical theories are applicable even to a fairly large molecule while the ab initio theories apply to a small-sized molecule. Both theories are now so well-established that no introduction to valence theory would be complete without some discussion on them. First, we shall discuss the semi-empirical theories based on the effective one-electron hamiltonian.

10.2 Extended Huckel Theory

The extended Hückel theory (EHT) proposed by Hoffmann[1] is an extension

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1. R. Hoffmann, *J. Chem. Phys.*, **39**, 1397, (1963).

of the simple Hückel theory allowing a treatment of both σ- and π-electrons in the same manner. It may be considered as a simple attempt to approximate the elements of a self-consistent field matrix $\hat{F}$ (Fock operator) in which only the valence electrons are considered. This method employs an effective one-electron hamiltonian but all the overlap integrals are retained. The EHT basis set is made up of Slater atomic orbitals for the valence electrons. Thus for hydrogen, only the 1*s*-orbital is considered, for lithium through fluorine, in the first row of the periodic table, the 2*s*- and 2*p*-orbitals are included; for the second row elements, one uses 3*s*, 3*p* and 3*d*-orbitals and sometimes 4*s*- and 4*p*-orbitals also. Each molecular orbital is written in the LCAO form as

$$\psi = \sum_{\nu} c_{i\nu}\phi_{\nu} \tag{10.1}$$

where $c_{i\nu}$ are the LCAO coefficients, ϕ_ν, ϕ_μ, etc., are the normalised Slater atomic orbitals (AO). On each centre, except the hydrogen atom, there is more than one AO such as s, p_x p_y, p_z, etc. Application of the variation theorem leads to a set of secular equations.

$$\sum_{\nu}(H_{\mu\nu} - \mathcal{E}_i S_{\mu\nu})c_{i\nu} = 0 \tag{10.2}$$

where i refers to the MOs and ν to the AOs; the $S_{\mu\nu}$ is the atomic orbital overlap integral and $\mathcal{E}_i$ is the energy of the ith MO. The matrix element $H_{\mu\nu}$ is defined by

$$H_{\mu\nu} = \langle \phi_\mu \mid H \mid \phi_\nu \rangle \tag{10.3}$$

Elimination of $c_{i\nu}$ in Eq. (10.2) leads to the typical secular determinant:

$$\begin{vmatrix} H_{11} - \mathcal{E} & H_{12} - S_{12}\mathcal{E} & H_{13} - S_{13}\mathcal{E} \ldots \\ H_{12} - \mathcal{E}S_{12} & H_{22} - \mathcal{E} & H_{23} - S_{23}\mathcal{E} \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{10.4}$$

The diagonal matrix elements $H_{\mu\mu}$ (or α_μ) are given by the negative of the valence state ionisation potential of the appropriate atomic orbital defined in Sec. 8.9. The off-diagonal elements $H_{\mu\nu}$ are taken proportional to the overlap, $S_{\mu\nu}$. A variety of expressions[2,3] are known for the off-diagonal elements. They are

$$H_{\mu\nu} = 0.5[H_{\mu\mu} + H_{\nu\nu}]S_{\mu\nu}K \tag{10.5}$$

$$H_{\mu\nu} = K'S_{\mu\nu}(H_{\mu\mu}\ H_{\nu\nu})^{1/2} \tag{10.6}$$

$$H_{\mu\nu} = S_{\mu\nu}[2 - \mid S_{\mu\nu} \mid] \times 0.5(H_{\mu\mu} + H_{\nu\nu}) \tag{10.7}$$

Equation (10.5) is usually used with a value of 1.75 for K. Equation (10.6) was given by Ballhausen and Gray for calculations of inorganic complexes.

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2. C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, **1**, 111, (1962).
3. L.C. Cusachs, *J. Chem. Phys.*, **43**, 5157, (1965).

Equation (10.7) is extensively used and given by Cusachs. The overlap integrals are calculated using Slater atomic orbitals and then the secular determinant is solved for the orbital energies and coefficients. The total energy is calculated by summing the energies of the occupied orbitals taking into account their occupancy numbers. Thus, for a closed shell system, the total electronic energy is given as

$$E_{\text{EHT}} = 2 \sum_{i}^{\text{occ.}} \mathcal{E}_i \tag{10.8}$$

The EHT is relatively successful in the qualitative prediction of preferred conformation of molecules. If the molecule contains several different atoms with widely diverse electronegativities, the use of the valence state ionisation potential as diagonal matrix elements results in an unbalanced charge distribution in which too much electron density is shifted toward the more electronegative centres. Such effect is not present in the SCF theory since a large build up of charge at a centre gives rise to an increase in electron-electron repulsion thus causing the electronegativity of the atom to decrease. Since EHT does not explicitly consider the electron-electron repulsion term, one can account for this term in an empirical manner, by allowing the diagonal matrix elements to be functions of the charge densities. This gives rise to the iterative extended Hückel theory. According to Rein et al.[4] the use of output charges from one iteration is the basis for the input matrix elements for the next iteration. They assumed a linear dependence of the ionisation potential 'α_μ' on the atomic charge density q_μ of the form $\alpha_\mu = \alpha_\mu^0 + \Delta\alpha_\mu q_\mu$. Here α_μ^0 and $\Delta\alpha_\mu$ are the input parameters. At each iteration α's are obtained from those of the previous cycle by equation

$$\alpha_\mu^{(n+1)} = (1 - \lambda)\alpha_\mu^{(n)} + \lambda(\alpha_\mu^{(o)} + q_\mu^{(n)}\Delta\alpha_\mu) \tag{10.9}$$

where $\lambda = 0.1$ and is known as the damping parameter. The use of the iterative method has been found to considerably smooth out the distribution of electron density leading to better agreement with SCF charge densities and good dipole moments.

10.3 Molecular Orbital Theory of Inorganic Complexes

One can apply the concept of EHT to the bonding in inorganic complexes. Crystal field theory is an incomplete theory of the structure and bonding because there are evidences from electron spin resonance spectroscopy that the valence electrons of the metal ion drift on to the ligands. Crystal field theory neglects the overlap between the ligand and the transition metal orbitals. If this overlap is taken into account then the LCAO method may be used to construct MOs of the complex. These orbitals are of the form

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[4] R. Rein, N. Fukuda, H. Win, G.A. Clarke, and F.E. Harris, *J. Chem. Phys.*, **45**, 4743, (1966).

$$\psi = \phi_M + \Sigma_i a_i\phi_i$$

where ϕ_M is the wavefunction of the metal atom and $\Sigma\, a_i\phi_i$ is the linear combination of the ligand wavefunctions, both transforming in the molecular point group as the same irreducible representation.

The valence atomic orbitals of the transition metal are usually taken to be nd, $(n + 1)s$, $(n + 1)p$. In the first transition series $n = 3$. The ligand valence atomic orbitals are usually the $2s$ and $2p$ orbitals. The problem of constructing MOs is very much simplified by the group theory. As an example, we consider an octahedral complex of the O_h symmetry. In order to construct molecular orbitals we shall first consider the orbitals of the ligands that are of the σ-type with respect to the particular M–L axis where M is the metal atom and L stands for the ligand atom. We shall label the σ-orbitals of the ligands with $\sigma_i(i = 1, 2, 3, \ldots 6)$, σ_i being the orbital of the i^{th} ligand (see Fig. 10.1) for an octahedral complex. We have seen in a previous chapter how the metal d-orbitals transform under the various operations of the O_h-group. The same procedure can be used for other orbitals of the metal atom. Thus, for the O_h-group, the metal atom orbitals transform as

$$\begin{array}{cccc} a_{1g} & t_{1u} & e_g & t_{2g} \\ s & \overbrace{p_x \quad p_y \quad p_z} & \overbrace{d_{z^2} \quad d_{x^2-y^2}} & \overbrace{d_{xy}, d_{yz}, d_{zx}} \end{array}$$

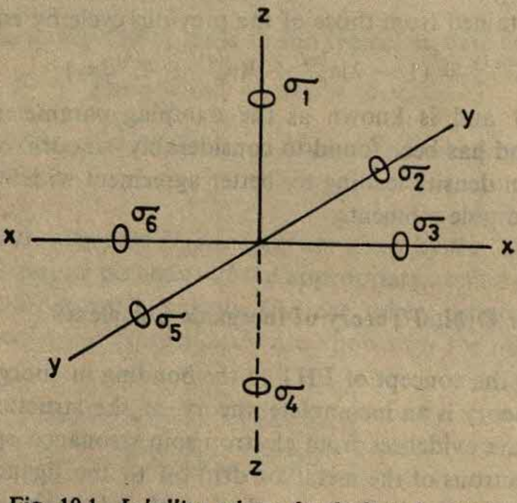


Fig. 10.1 *Labelling scheme for the ligand orbitals.*

We now turn to the ligand orbitals of the σ-symmetry made up of the $2s$ and $2p$-orbitals from each ligand pointing towards the metal atom. Using the method described in Chap. 9 we obtain the following characters of the representation

E	$6c_4$	$3c_2$	$6c_2'$	$8c_3$	i	$6s_4$	$3\sigma_h$	$6\sigma_d$	$8s_6$
6	2	2	0	0	0	0	4	2	0

This reducible representation has components $a_{1g} + e_g + t_{1u}$. The suitable linear combination of the ligand σ_l-orbitals are as follows.

$$\phi_1(a_{1g}) = \frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$

$$\phi_2(e_g) = \frac{1}{2}(\sigma_2 - \sigma_3 + \sigma_5 - \sigma_6)$$

$$\phi_3(e_g) = \frac{1}{\sqrt{12}}(2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6)$$

$$\phi_4(t_{1u}) = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_4)$$

$$\phi_5(t_{1u}) = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_5)$$

$$\phi_6(t_{1u}) = \frac{1}{\sqrt{2}}(\sigma_3 - \sigma_6)$$

where the σ_l-orbitals are shown in Fig. 10.1. These combinations of ligand orbitals are shown in Fig. 10.2 along with the atomic orbitals of the central metal atom with which they combine to form the MOs of the complex compounds. On account of the almost zero-overlap of the inter-ligand orbitals the energies of the above combinations of the ligand orbitals will be about the same and effectively equal to that of σ_1 alone. The resultant MOs will be as follows.

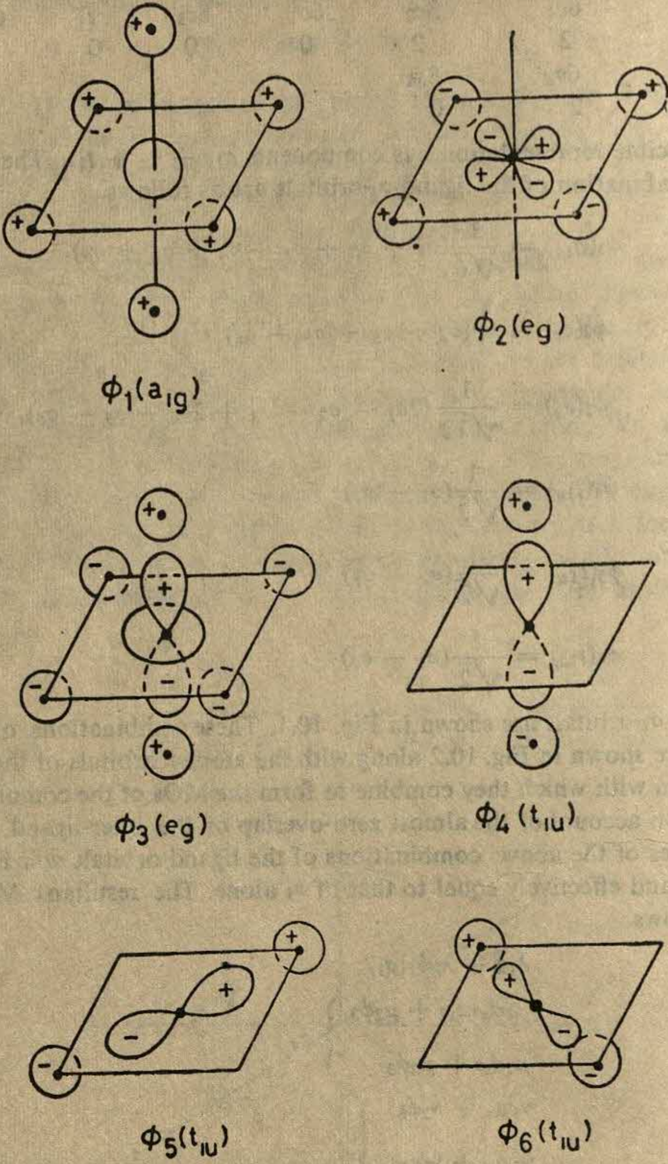
$$\lambda_1 s + \lambda_2\phi_1\}a_{1g}$$

$$\left.\begin{array}{l} \mu_1 d_{x^2-y^2} + \mu_2\phi_2 \\ \mu_1 d_{z^2} + \mu_2\phi_3 \end{array}\right\} e_g$$

$$\left.\begin{array}{l} \nu_1 p_x + \nu_2\phi_6 \\ \nu_1 p_y + \nu_2\phi_5 \\ \nu_1 p_z + \nu_2\phi_4 \end{array}\right\} t_{1u}$$

$$\left.\begin{array}{l} d_{xy} \\ d_{yz} \\ d_{xz} \end{array}\right\} t_{2g}$$

The numerical values of the coefficients λ, μ, ν can be determined by the variation method and by calculating the diagonal and off-diagonal matrix elements of H using the EHT-procedure. A typical situation is shown in



$\phi_1(a_{1g})$ $\phi_2(e_g)$

$\phi_3(e_g)$ $\phi_4(t_{1u})$

$\phi_5(t_{1u})$ $\phi_6(t_{1u})$

Fig. 10.2 *Appropriate combination of ligand orbitals with metal orbitals.*

Fig. 10.3 where the metal orbitals are on the left, the ligand group orbitals are on the right and in the middle there are full MOs. Since usually the ligand orbitals lie lower in energy than the metal orbitals we have drawn right hand energy levels below any of those on the left.

There are normally two electrons in each ligand orbital σ_i and according to Fig. 10.3 they will completely fill the three lowest levels which accommodate 12 electrons ($e_g^4 a_{1g}^2 t_{1u}^6$). Now these electrons can delocalise into the

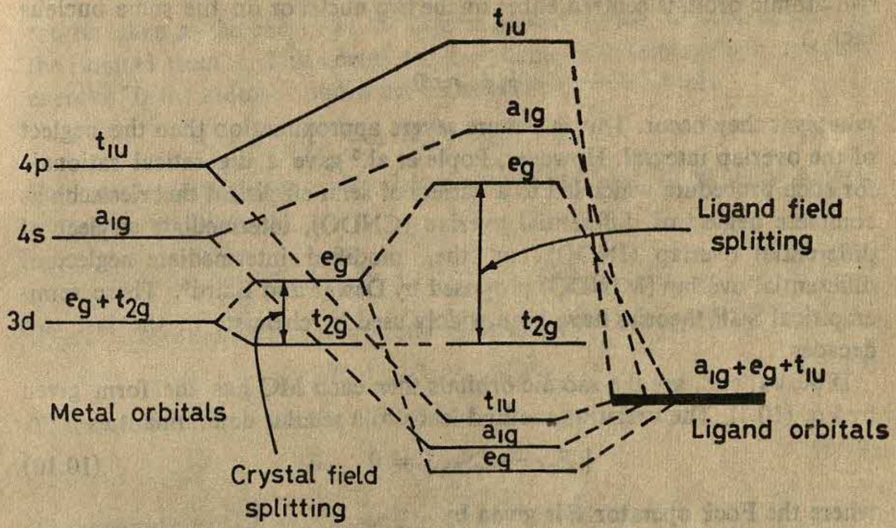


Fig. 10.3 *Energy levels of MOs in an octahedral complex related to those of the metal AOs (left) and the ligand group orbitals (right).*

metal atom orbitals. Similarly, the pure metal orbitals such as d_{z^2}, and $d_{x^2-y^2}$ will now have a fraction of the ligand orbitals. Since t_{2g} orbitals of the metal atom do not combine with the ligand orbitals, the separation Δ between the e_g and the t_{2g} orbitals of the metal is not the same as expected from crystal field theory alone. However, if the ligand orbitals lie much below the metal atom-d-orbitals then the e_g and t_{2g} orbitals correspond closely to those predicted on the crystal-field basis, because the interaction of the ligand orbitals with the metal orbitals becomes then negligible. The true description of the bonding in inorganic complexes is a mixture of the crystal field and molecular orbital descriptions. The theory just described is known as the ligand field theory. Although we have dealt with octahedral complex, these techniques may be extended to systems of different symmetry.

10.4 Semi-empirical SCF Theory

In semi-empirical SCF theories, one employs Roothaan's procedure as described in Chapter 8 to obtain self-consistent field molecular orbitals for all valence electrons. Pople, Santry and Segal[5] (1965) proposed an important method for all valence electron calculations in which they introduced zero-differential overlap approximation while some matrix elements of the Fock operator were determined by appeal to experimental data. The zero-differential overlap (ZDO) approximation means that if ϕ_μ and ϕ_ν are the two atomic orbitals centred either on the two nuclei or on the same nucleus then

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[5] J.A. Pople, D.P. Santry, and G.A. Segal, *J. Chem. Phys.*, 43, 5136, (1965); A comprehensive account is found in a book entitled "*Approximate Molecular Orbital Theory*" by J.A. Pople and D. Beveridge, McGraw-Hill (1970).

$$\phi_\mu \phi_\nu \approx 0$$

wherever they occur. This is a more severe approximation than the neglect of the overlap integral. However, Pople et al.[5] gave a theoretical rationale for such procedure which led to a variety of semi-empirical theories such as complete neglect of differential overlap (CNDO), intermediate neglect of differential overlap (INDO) and then modified intermediate neglect of differential overlap (MINDO) proposed by Dewar and Baird[6]. These semi-empirical SCF theories have been widely used by chemists in the last two decades.

If ϕ_ν, ϕ_μ, etc., are the atomic orbitals then each MO has the form given by Eq. (10.1). The variation method leads to a secular determinant as

$$| F_{\mu\nu} - ES_{\mu\nu} | = 0 \tag{10.10}$$

where the Fock operator $\hat{F}$ is given by

$$\hat{F} = \sum_{i}^{\text{all electrons}} H_i(\text{core}) + \sum_{j}^{\text{occ.MOs}} (2J_j - K_j) \tag{10.11}$$

The core hamiltonian $\hat{H}_i$ (core) for the i^{th} electron consists of the kinetic energy operator for the i^{th} electron and potential energy between that electron and all atomic cores of the molecule.

$$H_i\,(\text{core}) = -\frac{1}{2}\nabla_i^2 + \sum_A V_{A,i} \tag{10.12}$$

where $V_{A,i}$ is the electron-nuclear potential energy, i.e., $-Z_A/r_{Ai}, Z_A$ being the nuclear charge in atomic unit. We shall write the total core hamiltonian as

$$\begin{aligned} H^c &= \sum_i \hat{H}_i\,(\text{core}) = -1/2\nabla^2 + \sum_A V_A \\ &= -1/2\nabla^2 + V_A + \Sigma' V_B \end{aligned} \tag{10.13}$$

where we have separated the core potential of A from the remainder of the molecule. The prime in the above summation implies that the potential of A is excluded. The core hamiltonian integral $H^c_{\mu\mu}$ can be treated as

$$\begin{aligned} H^c_{\mu\mu} &= \langle \phi_\mu \mid \hat{H}^c \mid \phi_\mu \rangle \\ &= \langle \phi_\mu \mid -1/2\nabla^2 + V_A \mid \phi_\mu \rangle + \langle \phi_\mu \mid \sum_B{}' V_B \mid \phi_\mu \rangle \\ &= U_{\mu\mu} + \sum_B{}' \langle \phi_\mu \mid V_B \mid \phi_\mu \rangle \end{aligned} \tag{10.14}$$

where $A \neq B$ and

$$U_{\mu\mu} = \int \phi_\mu(-1/2\nabla^2 + V_A)\phi_\mu \, dv \tag{10.15}$$

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[6] N.C. Baird and M.J.S. Dewar, *J. Chem. Phys.*, **50**, 1262, (1969).

can be taken as the energy of the atomic orbital ϕ_μ for the valence state of the isolated atom A. This energy can be calculated in terms of spectroscopic energies. If the atoms A and B are far apart then the integral

$$\langle \phi_\mu \mid V_B \mid \phi_\mu \rangle = -Z_B \cdot R_{AB}^{-1} \text{ (in au)} \tag{10.16}$$

Pople assumed that two-centre electron-repulsion integrals at large separations are also given as

$$\langle \phi_\mu^A \phi_\mu^A \mid \phi_\nu^B \phi_\nu^B \rangle = \frac{1}{R_{AB}} = \gamma_{AB} \tag{10.17}$$

where ϕ_μ is centered on atom A and ϕ_ν on atom B. We can write

$$\langle \phi_\mu \mid V_B \mid \phi_\mu \rangle = -Z_B \gamma_{AB} \tag{10.18}$$

Therefore one may write Eq. (10.14) as

$$H^c_{\mu\mu} = U_{\mu\mu} - Z_B \gamma_{AB} \tag{10.19}$$

The integral over $(2\hat{J}_j - \hat{K}_j)$ [see Eq. 10.11] is given as

$$\begin{aligned} &\langle \phi_\mu \mid \sum_j^{\text{occ.MOs}} (2J_j - K_j) \mid \phi_\mu \rangle \\ &= \frac{1}{2} P_{\mu\mu} \gamma_{AA} + \sum_{\nu \neq \mu} P_{\nu\nu} \cdot \gamma_{AA} + \sum_{B \neq A} P_B \gamma_{AB} \end{aligned} \tag{10.20}$$

The derivation of Eq. (10.20) is the same as shown in Appendix 8, the difference being that Pople et al. used the notation P_A for electron densities on A. 'P_A' in all valence electron calculations is defined as

$$\left.\begin{aligned} P_A &= P_{\mu\mu} + \sum_{\nu \neq \mu} P_{\nu\nu} \\ P_{\mu\mu} &= 2 \sum_i^{\text{occ.MOs}} C_{i\mu} C_{i\mu} \end{aligned}\right\} \tag{10.21}$$

where both ϕ_μ and ϕ_ν are centred on A. The one-centre electron repulsion integral is defined as

$$\gamma_{AA} = \langle \phi_\mu \phi_\mu \mid \phi_\mu \phi_\mu \rangle$$

Pople assumed that one-centre repulsion integral, γ_{AA} had an average value characteristic of the atom regardless of the atomic orbitals, while the two-centre integral γ_{AB} was determined always by the interaction of two spherical orbitals (s-type Slater orbitals for the valence shell) located on the two nuclei.

Thus $F^A_{\mu\mu}$ where ϕ_μ is located on atom A is given as

$$F^A_{\mu\mu} = U_{\mu\mu} + \left(P_A - \frac{1}{2} P_{\mu\mu}\right) \cdot \gamma_{AA} + \sum_{B \neq A} (P_B - Z_B) \cdot \gamma_{AB} \tag{10.22}$$

Similarly one obtains

$$\left.\begin{aligned} F^A_{\mu\nu} &= -\frac{1}{2} P^A_{\mu\nu} \gamma_{AA} \\ P^A_{\mu\nu} &= 2 \sum^{\text{occ.MOs}} c_{i\mu} c_{i\nu} \end{aligned}\right\} \tag{10.23}$$

where both μ and ν-orbitals are centred on A, and

$$\left.\begin{aligned} F_{\mu\nu}^{AB} &= H_{\mu\nu}^{c} - \frac{1}{2} P_{\mu\nu}^{AB} \cdot \gamma_{AB} \\ P_{\mu\nu}^{AB} &= 2\sum_{i}^{\text{occ.MOs}} c_{i\mu} c_{i\nu} \end{aligned}\right. \tag{10.24}$$

where μ is located on A and ν on B.

In summary the CNDO approximations are as follows:

(1) Replace the overlap matrix by unit diagonal matrix and neglect all $S_{\mu\nu}$ in normalising the MOs.

(2) Neglect the differential overlap in all two-electron integrals, i.e.,

$$\langle \phi_\mu \phi_\nu \mid \phi_\rho \phi_\sigma \rangle = \langle \phi_\mu \phi_\mu \mid \phi_\rho \phi_\rho \rangle \delta_{\mu\nu} \delta_{\rho\sigma} = \gamma_{\mu\rho} = \gamma_{AB}$$

where ϕ_μ, ϕ_ν are centred on A, ϕ_ρ, ϕ_σ on B; and replace all such two-centre integrals by the integrals over s-type Slater orbitals, which are evaluated using the standard procedure.[7] Thus γ_{AB} becomes characteristic of the atom-pair for each value of internuclear separation.

(3) Neglect monoatomic differential overlap, i.e., $\langle \phi_\mu \mid H^c \mid \phi_\nu \rangle = 0$ if $\mu \neq \nu$ on atom A

(4) The integral $U_{\mu\mu}$ is chosen as the energy of the orbital ϕ_μ for the valence state of the atom on which the orbital is centred.

(5) Take $H_{\mu\nu}^{c}$ to be proportional to the overlap $S_{\mu\nu}$ as $H_{\mu\nu}^{c} = \frac{1}{2}(\beta_A^0 + \beta_B^0) \times S_{\mu\nu}$ where ϕ_μ is centred on 'A', and ϕ_ν on B.

Thus, the CNDO calculations require evaluation of the overlap integrals and γ_{AB} while the values of $U_{\mu\mu}$ and γ_{AA} as recommended by Sichel and Whitehead[8] are given in Table 10.1. The values of β_A^0 for the atoms of the first row in the periodic table were chosen by Pople and Segal.[9] We deal with the CNDO/2 method which is widely used. Values in Table 10.1 refer to those used in the CNDO/2 method.

TABLE 10.1 *Some Parameter Values in eV* for the CNDO/2 Calculations*

Atoms (A)	H	Li	Be	B	C	N	O	F
$U_{\mu\mu}(s)$	−13.6	−5.00	−15.54	−30.37	−50.69	−70.09	−101.31	−129.54
$U_{\mu\mu}(p)$	–	−3.67	−12.28	−24.70	−41.50	−57.85	−84.28	−108.93
β_{A}^{0}	− 9.0	−9.00	−13.00	−17.00	−21.00	−25 00	−31.00	−39.00
γ_{AA}	12.85	3.46	5.95	8.05	10.33	11.31	13.91	15.23

* (1 eV = 0.0368 au)

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[7] See for example, M. Kotani et al., *Tables of Molecular Integrals*, Maruzen and Co., Tokyo, 1955.

[8] J.M. Sichel and M.A. Whitehead, *Theo. Chem. Acta.*, **11**, 220, (1968).

[9] J.A. Pople and G.A. Segal, *J. Chem. Phys.*, **44**, 3289, (1966).

Since the CNDO/2 procedure is an iterative one, an initial estimate of the MO's is made by setting $F^{A}_{\mu\mu} = U_{\mu\mu}$, $F^{A}_{\mu\nu} = 0$, and $F^{AB}_{\mu\nu} = 1/2\,(\beta^{0}_{A} + \beta^{0}_{B}) \times S_{\mu\nu}$. Cycling then proceeds as in the SCF theory until the input and output eigenvectors agree to a predetermined accuracy.

10.5 Some Features and Comments on the CNDO Theory

In all valence-electron calculations besides the spherical orbitals (s-type), the directional atomic orbitals such as p_x, p_y, and p_z-orbitals are involved in addition to the angular dependent d-orbitals. If the full SCF calculations are performed without any approximations then the calculated energies and charge distributions will be the same whatever be the choice of coordinate axes for the basis orbitals. In other words, it should not matter how we choose the orientation of the directional orbitals like p, d, etc. If one wishes to make certain approximations to reduce the magnitude of calculations then the results of calculations become dependent on the choice of orientation of the orbital axes. The assumptions made by Pople et al. (see Sec. 10.4) had to be so designed as to make the resulting energies and charge distributions invariant to the choice of axes for the basis set atomic orbitals.

In EHT this is not a major problem even though the theory used both spherical and non-spherical atomic orbitals. In EHT the overlap integrals are only involved in calculation of the off-diagonal matrix elements of hamiltonian. Consider an interaction between an s-orbital on atom A and p_x-orbital on atom B as shown in Fig. 10.4 where

$$\langle s \mid p_{x_1} \rangle = S$$
$$\langle s \mid p_{y_1} \rangle = 0$$

Suppose the p_x-orbital on B is rotated by an angle θ in the $x - y$ plane. The transformation matrix equation is given as

$$\begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} \tag{10.25}$$

Now both p_{x_2} and p_{y_2} orbitals overlap with s-orbital on A.

$$\langle s \mid p_{x_2} \rangle = \cos\theta \langle s \mid p_{x_1} \rangle + \sin\theta \langle s \mid p_{y_1} \rangle$$
$$\langle s \mid p_{y_2} \rangle = -\sin\theta \langle s \mid p_{x_1} \rangle + \cos\theta \langle s \mid p_{y_1} \rangle$$

hence

$$\langle s \mid p_{x_2} \rangle^2 + \langle s \mid p_{y_2} \rangle^2 = (\cos^2\theta + \sin^2\theta) \langle s \mid p_{x_1} \rangle^2$$
$$+ (\cos^2\theta + \sin^2\theta) \langle s \mid p_{y_1} \rangle^2 = \langle s \mid p_{x_1} \rangle^2 = S^2 \tag{10.26}$$

Thus the sum of the square of the overlap remains the same whatever be the value of θ. Now consider the electron repulsion integral between an

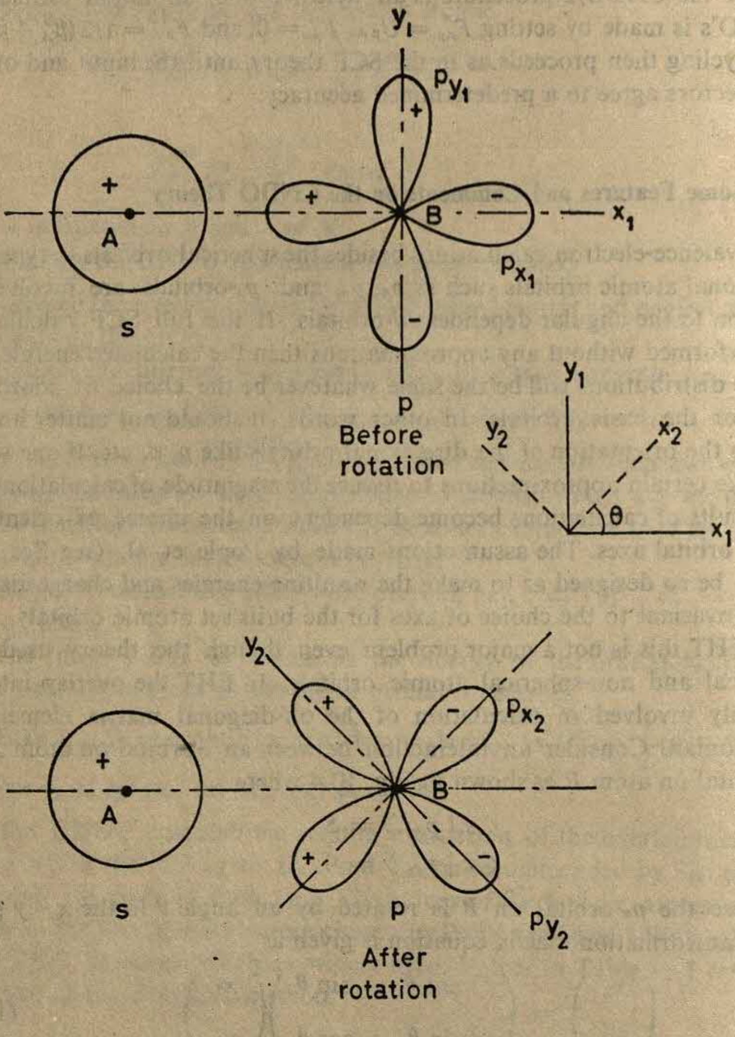

Fig. 10.4 *Interaction of an s-orbital with p_{x_1} orbital. The p_x- and p_y-orbitals are directed along the x- and y-axes. On the right hand side is shown the change of orientation of the X–Y axes.*

electron in an *s*-orbital on *A* and an electron in a p_{x_1}-orbital on *B*, i.e., $\langle s^A s^A \mid p^B_{x_1} p^B_{x_1} \rangle$.

If the orientation of the axes is changed by θ, then, following Eq. (10.25), we have

$$\begin{aligned}\langle s^A s^A \mid p^B_{x_2} p^B_{x_2} \rangle &= \cos^2\theta \, \langle s^A s^A \mid p^B_{x_1} p^B_{x_1} \rangle \\ &+ \sin^2\theta \, \langle s^A s^A \mid p^B_{y_1} p^B_{y_1} \rangle \\ &+ 2\cos\theta \sin\theta \, \langle s^A s^A \mid p^B_{x_1} p^B_{y_1} \rangle \qquad (10.27)\end{aligned}$$

In the ZDO approximation the last term of Eq. (10.27) vanishes because p_x and p_y are orthogonal. We, therefore, have

$$\langle s^A s^A \mid p^B_{x_2} p^B_{x_2} \rangle = \cos^2\theta \langle s^A s^A \mid p^B_{x_1} p^B_{x_1} \rangle + \sin^2\theta \langle s^A s^A \mid p^B_{y_1} p^B_{y_1} \rangle \tag{10.28}$$

In order to make the electron-repulsion integral on the left hand side of Eq. (10.28) independent of the orientation of axes Pople et al. assumed

$$\langle s^A s^A \mid p^B_x p^B_x \rangle = \langle s^A s^A \mid p^B_y p^B_y \rangle = \langle p^A_x p^A_x \mid p^B_y p^B_y \rangle = \langle s^A s^A \mid s^B s^B \rangle \tag{10.29}$$

where s^B is the spherical orbital with the same radial function as p^B. In other words, both s and p-orbitals of the same atom have the same orbital exponent. This ensures that results of the CNDO calculations remain invariant not only to choice of coordinate axes of the atomic orbitals but also to hybridisation.

In the CNDO calculations sometimes two-centre repulsion integrals are estimated from the Mataga-Nishimoto formula[10], i.e.,

$$\gamma_{AB} = 1/(R + a_{AB}) \tag{10.30}$$

where R is the separation of atoms in atomic units and

$$a_{AB} = 2/(\gamma_{AA} + \gamma_{BB}) \tag{10.31}$$

where the values of γ are to be expressed in atomic unit. Once again the invariance to the choice of axes is ensured by the above equations.

There is another feature in the CNDO theory that ought to be mentioned. The matrix elements of $\hat{F}$ consist of two parts: the matrix element of $\hat{H}$ (core) representing an overall attractive potential and the matrix element of $(2\hat{J}_i - \hat{K}_i)$ offering repulsive potential. Similar degrees of approximation ought to be made in both parts of the Fock operator. This is true when the diagonal elements of $\hat{F}$ are computed according to the method prescribed by Pople et al. However, this is not true for the off-diagonal elements F_{μ}^{AB}. According to the CNDO method, $F_{\mu\nu}^{AB}$ is given by Eq. (10.24) where in $H^c_{\mu\nu}$ the bicentric overlap integral is retained while it is completely neglected in the electron-repulsion integrals by enforcing the ZDO approximation. This is not a rational approach as far as the theory is concerned. Bhattacharya and Chowdhury[11] examined this point and came up with a variable β-CNDO method. However, when they tested their method on some heteronuclear diatomic species they found that the values of β converged to the starting values after several iterations. Their results therefore support the use of nonvariable β-approximation as prescribed by Pople et al. earlier.

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[10] N. Mataga and K. Nishimoto, *Z. Physik Chem.* (*Frankfurt*), **12**, 335; **13**, 140, (1957).

[11] S.P. Bhattacharya and M. Chowdhury, *J. Phys. Chem.*, **81**, 1598, (1977).

In the CNDO calculations average values of γ_{AA} and γ_{AB} are used irrespective of the atomic orbitals concerned. This is certainly a poor approximation. An alternative procedure using hybrid orbitals has been examined by Cook, Hollis and McWeeny[12]. Since the hybrids tend to be localised in different regions of space, the validity of the ZDO approximation is enhanced. Calculations using hybrid orbitals and with parameters computed non-empirically yield results close to those based on the fitting of experimental data. This lends a general support to the CNDO type of formalism in the MO theory.

It should be remembered that in all valence electron calculations the orbitals of the core electrons in each atom are ignored in the construction of the MOs. This means that the coulomb (J) and exchange (K) integrals between core and valence electrons are always neglected in the CNDO theory.

10.6 Applications of the CNDO Procedure

There were various modifications of the CNDO-method so far as the values of the parameters were concerned. Wilberg[13] adopted the CNDO/2 procedure with some modified values of the parameters $U_{\mu\mu}$ and β_A^0 to obtain the heats of atomisation of some hydrocarbons. While Pople and Segal[9] predicted the equilibrium geometries of some common molecules, Sichel and Whitehead[8] with their parameters (Table 1) were able to improve on the binding energies obtained by Pople and Segal. Attempts to predict electronic spectra by the original CNDO/2 method were rather unsuccessful. CNDO/2 method gave excitation energies that were too high. Besides, in view of the neglect of the differential overlap, the singlet and the corresponding triplet states have the same energies. Del Bene and Jaffe[14] developed a successful CNDO-treatment of the excited states which involved configuration interaction. The results are generally satisfactory. Generally the CNDO-procedures gave ionisation potentials that were higher than the experimental values and sometimes predicted an incorrect ordering of orbital energies. This deficiency was independent of the parameter sets used. Pople and Gordon[15] have used the CNDO method to calculate the dipole moments of a large number of organic molecules and achieved a reasonable degree of success. The fact that dipole moments are fairly well reproduced by the CNDO method has been substantiated by other authors also. In the area of hydrogen bonding the CNDO/2 method has achieved some success. Murthy and Rao[16] studied hydrogen bonding in water dimer using both EHT and CNDO/2 methods and concluded that the latter method gave reasonable results. Hoyland and Kier[17] have studied hydrogen bonding in other molecules with encouraging esults. Hermann[18] considered electrophilic substitution reaction in pyrrole, indole, furan, and benzofuran utilising both EHT and CNDO/2 procedures. He considered a proton as the electrophile. Both methods predict the preferred position of attack, but only CNDO/2 accounts well for the relative basicity of various positions of indole.

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[12] D.B. Cook, P.C. Hollis and R. McWeeny, *Mol. Phys.*, **13**, 553, (1967).

[13] K.B. Wilberg, *J. Am. Chem. Soc.*, **90**, 59, (1968).

[14] J. Del Bene and H.H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050, (1968); 49, 1221, (1968).

[15] J.A. Pople and M.S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253, (1967).

[16] A.S.N. Murthy and C.N.R. Rao, *Chem. Phys. Letts.*, **2**, 123, (1968).

10.7 INDO and MINDO Methods

Dixon[19] and Pople et al.[20] have proposed a modification of the CNDO method. They have called it INDO (intermediate neglect of differential overlap) which uses the basic assumptions of CNDO but differs from it in the non-neglect of one-centre electron repulsion integrals of the form $\langle \mu\nu/\mu\nu \rangle$ where both μ and ν-orbitals are centred on the same atom. This modification was prompted by the fact that one could not obtain any singlet-triplet splittings in the excited states by the CNDO method. The inclusion of the above type one-centre integrals means that more integrals are to be considered in the INDO method. These integrals were expressed by Pople et al. in terms of the Slater-Condon parameters (F^N, G^N), which could be obtained from spectral data. The INDO method predicts molecular geometries as good as, if not better than, CNDO/2 method and the computed dipole moments are also improved.

A method similar to INDO was later developed by Dewar and coworkers[6] for computing heats of formation. This method has been designated as MINDO (modified INDO), whose aim was to get the best fit to experimental data, while the objective of Pople's CNDO methods was to reproduce the results of ab initio SCF calculations using the same set of atomic orbitals. The MINDO method was subsequently improved by Dewar and his coworkers and known in the literature as MINDO/2 and MINDO/3 methods. A detailed discussion is outside the scope of this book. The interested readers are advised to consult the original papers[21].

10.8 Use of Gaussian Orbitals in Non-Empirical Methods

For many years the semiempirical MO methods were used for the treatment of polyatomic molecules. They certainly provided an understanding of chemical phenomena and gave a conceptual framework. But a carefully parameterised theory may give results whose agreement with experimental data may be fortuitous. In view of the large scale use and the availability of computers one may be tempted to attempt at the nonempirical or ab initio calculations of molecules. By ab initio it means that no approximation is involved in the SCF calculations though the method itself is a mere approximation to the solution of the Schrödinger equation.

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[17] J.R. Hoyland and L.B. Kier, *Theo. Chim. Acta.*, **15**, 1, (1969).

[18] R.B. Herman, *Int. J. Quantum. Chem.*, **2**, 165, (1968).

[19] R.N. Dixon, *Mol. Phys.*, **12**, 83, (1967).

[20] J.A. Pople, D.L. Beveridge and P.A. Dobosh, *J. Chem. Phys.*, **47**, 2026, (1967).

[21] M.J.S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590, (1970); R.C. Bingham, M.J.S. Dewar and D.H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307, (1975).

Ab initio calculations using Slater-type of atomic orbitals were reported in the literature for many diatomic molecules. Extension of these calculations to polyatomic molecules is time consuming because of the difficulty of the evaluation of the two-electron integrals. Boys[22] proposed the use of Gaussian type of atomic orbitals which are given in the Cartesian form as

$$\chi_{n,l,m}\,(s, y, z, \alpha) = N_\alpha x^l y^m z^n \exp\,(-\alpha r^2) \tag{10.32}$$

where the spherical harmonics are replaced by the cubic harmonics. Boys suggested that each MO can be constructed from a linear combination of Gaussian atomic orbitals. The advantage of such functions is that the multicentre integrals which we come across in treatment of polyatomic molecules can be easily evaluated.

In a MO calculation of polyatomic molecules the most difficult integral to evaluate is the four-centre two-electron repulsion integrals like

$$\langle\, \phi_\mu \phi_\nu \mid \phi_\rho \phi_\sigma \,\rangle$$

where μ, ν, ρ and σ are the different nuclear centres. If the atomic orbitals are of the Gaussian forms, i.e., $\exp\,(-\alpha r^2)$ then the product of two Gaussians on different centres is a Gaussian about the third centre. For example, we suppose a Gaussian orbital centred at the origin and another Gaussian orbital at a distance 's' from the origin. The product of the two Gaussian orbitals may be given as

$$\begin{aligned}
&\exp\,(-\alpha r^2)\exp\,[-\alpha'(s-r)^2] \\
&\quad = \exp\,[-(\alpha r^2 + \alpha' s^2 + \alpha' r^2 - 2\alpha' s r)] \\
&\quad = \exp\,[-(\alpha+\alpha')r^2 - 2\alpha' s r + \alpha' s^2] \\
&\quad = \exp\,[-(\alpha+\alpha')\,\{r^2 - 2\lambda s r + \lambda s^2\}] \text{ where } \lambda = \frac{\alpha'}{\alpha+\alpha'} \\
&\quad = \exp\,[-(\alpha+\alpha')\,\{(r^2 - 2\lambda s r + \lambda^2 s^2) - (\lambda^2 s^2 - \lambda s^2)\}] \\
&\quad = \exp\,[-(\alpha+\alpha')(r-\lambda s)^2]\cdot\exp\,[(\alpha+\alpha')s^2\lambda(\lambda-1)] \\
&\quad = \exp\,[-(\alpha+\alpha')(r-\lambda s)^2]\cdot\exp\,[s^2\alpha'\{-\alpha/(\alpha+\alpha')\}] \\
&\quad = A\exp\,[-(\alpha+\alpha')(r-\lambda s)^2]
\end{aligned} \tag{10.33}$$

where $A = \exp\left[-\dfrac{\alpha\alpha' s^2}{\alpha+\alpha'}\right]$

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[22] S.F. Boys, *Proc. Roy. Soc. A.*, **200**, 542, (1950).

Above equation shows that the product of two Gaussians is a new Gaussian whose centre is displaced by λs from the origin. It follows therefore that in a Gaussian expansion all the multicentred integrals can be reduced to two-centre integrals which are relatively easy to evaluate and much less time-consuming.

However, there are disadvantages. Boys prescribed that many Gaussian-type of orbitals (GTO) were needed to obtain for atoms the same degree of accuracy as the Slater-type of orbitals (STO). Another disadvantage of the GTO is the absence of cusps in the orbital. For the 1s-type function $l = m = n = 0$ in Eq. (10.32), one obtains

$$\frac{d\chi}{dr} = N_\alpha \exp(-\alpha r^2)(-2\alpha r) = 0 \text{ (at } r = 0) \tag{10.34}$$

while for the 1s—STO

$$\frac{d\chi}{dr} = N_\alpha \exp(-\alpha r)(-\alpha) \neq 0 \text{ (at } r = 0) \tag{10.35}$$

Since STOs are the natural solutions of the central-field problem, GTOs cannot describe properties relying on wavefunctions close to the nucleus. But the advantage of evaluating the multicentred integrals outweighs the disadvantages mentioned above and the ab initio calculations involving GTOs are now widely used in molecular physics.

10.9 Ab Initio MO Methods

Pople et al.[23] arrived at well defined ab initio methods at different levels of accuracy which are simple enough to be applied systematically to moderately large organic molecules. The basic premise of their method is that each STO is replaced by a finite Gaussian expansion. The results approach those of the full Slater-type calculations as the size of the Gaussian set increases.

Consider a 1s Slater type of atomic orbital of a hydrogen atom, i.e., $\psi_s \approx 1/\sqrt{\pi} \exp(-r)$. The corresponding energy is -0.5 a.u. A normalised Gaussian orbital of a hydrogen atom is given as

$$\psi_1 = N_\alpha \exp(-\alpha r^2) \tag{10.36}$$

If the energy is minimised by varying α by the variation method then one obtains

$$\alpha = 0.283$$

$$\psi_1 = 0.2765 \exp(-0.283 r^2)$$

$$E_1 = -0.424 \text{ au}$$

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[23] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.*, **51**, 2657, (1969); R. Ditchfield, W.J. Hehre and J.A. Pople, *J. Chem. Phys.*, **54**, 724, (1971).

In Fig. 10.5 are shown the variations of ψ_s and ψ_1 with r. It shows that ψ_1 does not fit ψ_s properly both at small and large values of r. The best way to improve this approximate function ψ_1 is to add new Gaussian functions at places where ψ_1 behaves poorly. Consider ψ_2

$$\psi_2 = c_1 N_\alpha \exp(-\alpha r^2) + c_2 N_\beta \exp(-\beta r^2) \tag{10.37}$$

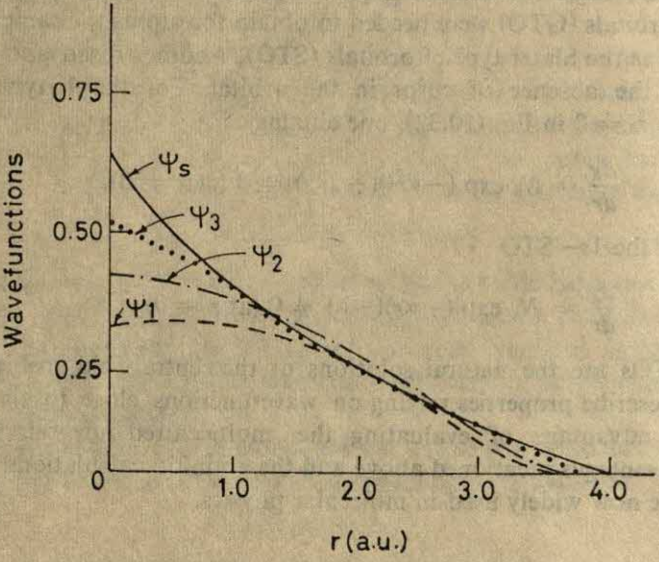

Fig. 10.5 *Variation with r of ψ_s, ψ_1, ψ_2 and ψ_3. All quantities are in atomic unit.*

The energy of ψ_2 is again given by $H\psi_2 = E_2\psi_2$ where the linear coefficients c_1, c_2 and the nonlinear coefficients α and β are varied to minimise the energy. Pople et al. found the following values

$$c_1 = 0.2744, \qquad c_2 = 0.8212$$
$$\alpha = 1.33 \qquad \beta = 0.201$$

and $E_2 = -0.4858$ au which is better than E_1. Later, Pople et al. chose three Gaussians in the expansion as

$$\psi_3 = c_1 N_\alpha \exp(-\alpha r^2) + c_2 N_\beta \exp(-\beta r^2) + c_3 N \exp(-\gamma r^2) \tag{10.38}$$

They minimised the energy by varying both the linear and nonlinear coefficients. The optimum values of the parameters of Eq. (10.38) are

$$\alpha = 2.2276, \qquad \beta = 0.4058, \qquad \gamma = 0.1098$$
$$c_1 = 0.1543, \qquad c_2 = 0.5353, \qquad c_3 = 0.4446$$

The energy obtained for the hydrogen atom is -0.4949 au which is closer to the exact value. Figure (10.5) also shows that ψ_3 fits well with ψ_s both near the nucleus and far away from it.

Pople et al. used a convention for basis sets. Their basis sets at the minimum level are called STO-NG meaning any STO is fitted by N-Gaussians on each atom. The most popular in the MO calculations is the STO-3G basis set. Pople et al. later extended the basis sets at the double zeta level through the use of STO-*lmn*G where *l*, *m*, *n* indicate respectively the number of Gaussian functions fitting the core orbitals, the inner valence, and the outer valence orbitals of the atom. For example, the 4-31G basis of carbon contains 4-Gaussians describing the 1*s* orbital, 3-Gaussians describing a set of 2*s*- and 2*p*-orbitals while the second set of 2*s* and 2*p*-orbitals contains a single Gaussian function. The 6-31G basis set differs from the 4-31G basis in improvement of the core orbitals of the atom. Further, polarisation of the basis set of atomic orbitals is indicated by an asterisk(*) when a set of d-functions are added to the heavy atom. When the double asterisk(**) is used it means a set of *d*-functions for the heavy atom and a set of *p*-functions for the hydrogen atoms. Examples are STO-3G*, 4-31G*, 6-31G*, 6-31G**. An extensive review of ab initio methods and its applications can be found in reference 24 and 25.

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[24] P. Carsky and M. Urban, "Ab Initio Calculations. *Methods and Applications in Chemistry*", Springer Verlag, Berlin, (1980).

[25] Shavitt in "*Methods of Computational Physics*", edited by B. Alder et al., Academic Press, New York, Vol. 2, (1965).

11

Hellmann-Feynman Theorem and Its Chemical Applications

11.1 Introduction

Chemists are generally familiar with the energy concept in molecular quantum mechanics. As a result, almost every phenomenon in chemistry is discussed in terms of the energy, such as, potential energy diagrams, correlation diagrams, activation energy, etc. But such concepts have not always proved to be very satisfactory in chemistry because they lack the simplicity and the elegant nature. Chemists always look for a simpler concept to work with. Such concepts or any model based on such concept should not only be capable of explaining, without much efforts, the various chemical phenomena such as the nature of chemical bonding, change of shape of molecules on excitation, chemical reactions, etc., but also withstand the critical examination of a theorist. One such concept was provided by the two physicists, namely, H. Hellmann[1] and R.P. Feynman[2] who discovered that if the three dimensional charge distribution in a system of electrons and nuclei were known from a quantum mechanical procedure, the actual force on any nucleus can be interpreted in terms of the classical electrostatics. Or in terms of fields, the force on a nucleus is the charge on that nucleus times the electric field due to all electrons and other nuclei. Feynman[2] further says "a three dimensional electron cloud in a molecule is prevented from collapsing by obeying the Schrödinger equation".

The above statement (or statements) in regard to the force on a nucleus in a molecule was challenged by Coulson and Bell[3] but Berlin[4] showed that this challenge arose from a misunderstanding and gave a further proof of the theorem and a more clear interpretation of the electrostatic approach. Hurley[5] gave the best theoretical justification of the actual use of such

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1. H. Hellmann, *Einfurhrung in die Quanten Chemie*, 285, Leipzig, (1937).
2. R.P. Feynman, *Physical Review*, **56**, 340, (1939).
3. C.A. Coulson and R.P. Bell, *Trans, Farad. Soc.*, **41**, 141, (1945).
4. T. Berlin, *J. Chem. Phys.*, **19**, 208, (1951).
5. A.C. Hurley, *Proc. Roy. Soc. A*, **226**, 170, 179, (1954): *Proc. Roy. Soc. A*, **235**, 224, (1956).

electrostatic approach. He shows that the force calculations are valid even for approximate wavefunctions. That is why the force approach has been extensively used by various authors in the last two decades to derive informations of chemical interest. Our primary motivation for studying the force concept in this chapter is to see what gains in physical insight result from an application of this conceptually simple tool.

11.2 The Hellmann-Feynman Theorem

This theorem states that if ψ is an exact (unnormalised) wavefunction of a Hamiltonian H and E the corresponding eigenvalue then for any parameter α on which the Hamiltonian depends

$$\frac{dE}{d\alpha}\langle\psi\mid\psi\rangle=\left\langle\psi\left|\frac{dH}{d\alpha}\right|\psi\right\rangle \tag{11.1}$$

Thus, depending on the nature of the parameter α which may be nuclear charge, nuclear coordinate, etc. we obtain valuable information about the variations in energy during molecular processes. The proof of the above theorem is simple. We start by writing

$$E\langle\psi\mid\psi\rangle=\langle\psi\mid\hat{H}\mid\psi\rangle \tag{11.2}$$

and then differentiate Eq. (11.2) with respect to α getting

$$\begin{aligned}\frac{dE}{d\alpha}\langle\psi\mid\psi\rangle+E\left\langle\frac{d\psi}{d\alpha}\mid\psi\right\rangle+E\left\langle\psi\mid\frac{d\psi}{d\alpha}\right\rangle\\=\left\langle\psi\left|\frac{dH}{d\alpha}\right|\psi\right\rangle+\left\langle\frac{d\psi}{d\alpha}\mid\hat{H}\mid\psi\right\rangle+\left\langle\psi\mid\hat{H}\mid\frac{d\psi}{d\alpha}\right\rangle\end{aligned} \tag{11.3}$$

Since H is hermitian and ψ is an exact solution of $\hat{H}\psi=E\psi$, we have

$$\left\langle\psi\mid\hat{H}\mid\frac{d\psi}{d\alpha}\right\rangle=\left\langle\frac{d\psi}{d\alpha}\mid\hat{H}\mid\psi\right\rangle=E\left\langle\frac{d\psi}{d\alpha}\mid\psi\right\rangle \tag{11.4}$$

Equation (11.1) follows immediately. Although the theorem is derived for exact wavefunctions it can be shown to be valid for approximate wavefunctions. Hurley[5] assumed a dependence of the approximate wavefunction ψ on α through some parameters $\lambda_1, \lambda_2, \ldots \lambda_n$. Suppose we have an approximate wavefunction ψ given as

$$\psi=\psi(\lambda_1,\lambda_2,\lambda_3,\ldots\lambda_n) \tag{11.5}$$

Examples of these parameters λ_i for the LCAO type of wavefunctions are the linear coefficients of atomic orbitals, orbital exponents, etc. The value of these parameters may depend on α (nuclear coordinate) as

$$\lambda_i=\lambda_i(\alpha) \tag{11.6}$$

Then the dependence of ψ on α is reflected in the way λ_i's change with α. We may therefore write the energy of the system calculated from ψ as

$$E(\alpha)=\epsilon(\lambda_i,\alpha)=\langle\psi(\lambda_i)\mid H(\alpha)\mid\psi(\lambda_i)\rangle \tag{11.7}$$

Differentiating Eq. (11.7) with respect to α gives

$$\frac{dE(\alpha)}{d\alpha} = \frac{\partial \epsilon}{\partial \alpha}(\lambda_i, \alpha) + \sum_i \frac{\partial \epsilon}{\partial \lambda_i}(\lambda_i, \alpha)\frac{\partial \lambda_i}{\partial \alpha}$$

$$= \left\langle \psi(\lambda_i) \left| \frac{\partial H}{\partial \alpha} \right| \psi(\lambda_i) \right\rangle + \sum_i \frac{\partial \epsilon}{\partial \lambda_i}(\lambda_i, \alpha)\cdot\frac{\partial \lambda_i}{\partial \alpha} \tag{11.8}$$

If the second part on the right hand side of Eq. (11.8) vanishes we obtain the Hellmann-Feynman (H–F) theorem.

This shows that the H–F theorem is valid for approximate wavefunctions $\psi(\lambda_i)$ if

either $$\frac{\partial \epsilon}{\partial \lambda_i}(\lambda_i, \alpha) = 0 \tag{11.9}$$

or $$\frac{\partial \lambda_i}{\partial \alpha} = 0 \tag{11.10}$$

For floating type of wavefunctions $\partial\lambda_i/\partial\alpha = 0$ as the parameters λ_1, λ_2, λ_3 . . . etc., are independent of the nuclear coordinate α. Equation (11.9) suggests that if the parameters λ_i, etc., in the approximate function ψ are adjusted to minimise $\epsilon(\lambda_i, \alpha)$ for any particular value of α the H–F theorem is obeyed. This means that the approximate wavefunctions which are obtained using the variation principle satisfy the H–F theorem.

11.3 Electrostatic Force and Its Advantages

We shall now show how the net force on a nucleus in a molecule is obtained. Consider a diatomic molecule AB. We assume that we shall be working within the Born-Oppenheimer approximation, i.e. we shall take the nuclear and electronic coordinates to be mutually independent. If X_A be the x-coordinate of the A^{th} nucleus, then the x-component of the force on the same nucleus wlll be given by $-\partial E/\partial X_A$. Since $\hat{H} = \hat{T} + \hat{V}$, where the electronic kinetic energy operator $\hat{T}$ is independent of nuclear coordinates, one can write for a normalised wavefunction ψ, (using the H–F theorem Eq. 11.1),

$$F_{Ax} = -\frac{\partial E}{\partial X_A} = -\left\langle \psi \left| \frac{\partial V}{\partial X_A} \right| \psi \right\rangle \tag{11.11}$$

where the potential function V consists of three parts, i.e.

$$V = V_{ee} + V_{nn} + V_{en}$$

The electronic repulsion term, V_{ee} is independent of the nuclear coordinates. The nuclear repulsion term V_{nn} and the electron nuclear interaction term, V_{en} are given by (in atomic unit)

$$V_{nn} = \frac{Z_A Z_B}{R} \tag{11.12}$$

$$V_{en} = -\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} \tag{11.13}$$

where Z's are the nuclear charges, R, the internuclear distance, r_{Ai} and r_{Bi} are the distances of an i^{th} electron from nuclei A and B respectively. Let us assume that the direction of the bond $A-B$ is along the x-axis (Fig. 11.1).

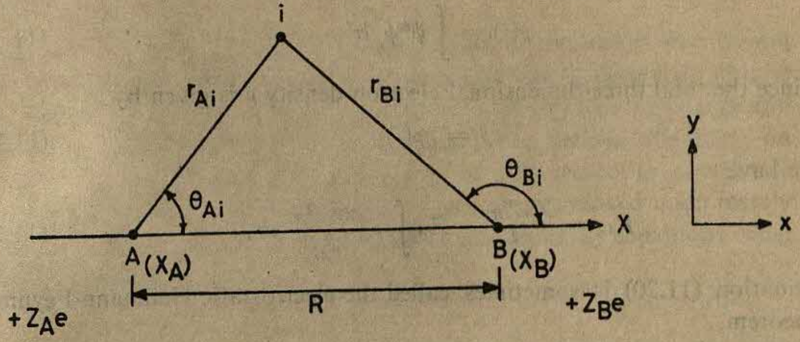

Fig. 11.1 *The coordinates of electron and nuclei in a molecule AB.*

Then

$$R = X_A - X_B \qquad r_{Ai} = r_A - r_i$$

$$\frac{\partial r_{Ai}}{\partial X_A} = \frac{X_{Ai}}{r_{Ai}} = \cos\theta_{Ai} \qquad \frac{\partial r_{Bi}}{\partial X_A} = 0$$

$$\frac{\partial V_{nn}}{\partial X_A} = -\frac{Z_A Z_B}{R^2} \tag{11.14}$$

$$\frac{\partial V_{en}}{\partial X_A} = -\frac{\partial}{\partial X_A}\left(\sum_i \frac{Z_A}{r_{Ai}}\right) = Z_A \sum \frac{1}{r_A^2}\frac{\partial r_{Ai}}{\partial X_A}$$

$$= Z_A \sum \frac{\cos\theta_{Ai}}{r_{Ai}^2} \tag{11.15}$$

where θ_{Ai} is the angle between the x-axis and the vector from electron i to nucleus A.

Therefore, the net force on a nucleus A along the bond follows from Eqs. (11.11), (11.14) and (11.15)

$$F_{Ax} = -\frac{\partial E}{\partial X_A} = -\left\langle \psi^* \left| \frac{\partial V_{nn}}{\partial X_A} + \frac{\partial V_{en}}{\partial X_A} \right| \psi \right\rangle$$

$$= \frac{Z_A Z_B}{R^2} - Z_A \left\langle \psi^* \left| \sum_i \frac{\cos\theta_{Ai}}{r_{Ai}^2} \right| \psi \right\rangle$$

$$= \frac{Z_A Z_B}{R^2} - Z_A \int \sum_i \frac{\cos\theta_{Ai}}{r_{Ai}^2}\left[\int \psi^*\psi \, d\tau'\right] d\tau_i \tag{11.16}$$

where $d\tau'$ refers to the integration over the coordinates of all electrons except the i^{th} electron and $d\tau_i$ refers to the coordinates of the i^{th} electron.

Let there be n electrons in a molecule. For each electron the term $\cos\theta_{Ai}/r_{Ai}^2$ in the summation of Eq. (11.16) is the same. Therefore,

$$F_{Ax} = \frac{Z_A Z_B}{R^2} - Z_A \int n \frac{\cos\theta_{Ai}}{r_{Ai}^2} \rho(i)\, d\tau_i \tag{11.17}$$

where the one-electron density function $\rho(i)$ is defined as

$$\rho(i) = \int \psi^* \psi\, d\tau' \tag{11.18}$$

Since the total three-dimensional electron density ρ is given by

$$\rho = n\rho(i) \tag{11.19}$$

we have

$$F_{Ax} = \frac{Z_A Z_B}{R^2} - Z_A \int \rho \frac{\cos\theta_{Ai}}{r_{Ai}^2}\, d\tau_i \tag{11.20}$$

Equation (11.20) is sometimes called the electrostatic Hellmann-Feynman theorem.

Thus, the net force on a nucleus is simply the resultant of the repulsive forces due to the other nuclei [the first term in Eq. (11.20)] and the attractive forces due to the surrounding electronic distribution [the second term in Eq. (11.20)]. These forces are obtained by the classical electrostatic method if the charge distributions in a molecule are accurately known. If the wavefunctions of a diatomic molecule are known for various internuclear separations, Eq. (11.20) permits one to calculate the corresponding forces on a nucleus and determine the equilibrium separation where there is no net force on a nucleus. Since $F_{Ax} = -(\partial E/\partial X_A)$ it is easy to visualise that the configuration where the net force is zero corresponds to the energy minimum. Although we have derived the electrostatic Hellmann-Feynman theorem for diatomic molecules the derivation can be extended to the case of polyatomic molecules.

The concept of electrostatic force has certain advantages over the concept of total energy even though calculation of force always involves an approximate density function. One is the computational advantage. If we use the molecular orbital method for obtaining the charge density, the total density is given by

$$\rho(r) = \sum_i^{\text{occ}} n_i \psi_i^2 \tag{11.21}$$

where ψ_i is the i^{th} MO and n_i is its occupation number. One can write Eq. (11.20) as

$$F_A = \frac{Z_A Z_B}{R^2} - Z_A \sum_i^{\text{occ}} n_i \int \psi_i^2 \frac{\cos\theta_{Ai}}{r_{Ai}^2}\, d\tau_i \tag{11.22}$$

Equation (11.22) shows that the total force on a nucleus is a simple sum of the orbital contributions. But the total energy is not a sum of the orbital energies.

The second advantage is that force is an expectation value of an one-electron operator. It is more sensitive to any change in wavefunctions than the energy. Hence, the force varies more drastically with the change in molecular geometry than does the energy which is relatively insensitive to change in the molecular shape. The prediction of molecular shapes is likely to be more accurate on the basis of the electrostatic force than on the total energy.

In spite of these advantages, the concept of the electrostatic force did not receive in the past as much attention in chemistry as it deserved. This is mainly because the force is not an observable quantity like the energy and not even a quantum mechanical constant of motion. Besides, the force on a nucleus in a molecule is not always invariant with respect to coordinate transformation whereas the energy is. So, it was always looked upon merely as a gradient of the potential energy rather than a quantity capable of being derived independently.

11.4 A Physical Picture of the Chemical Bond from the Force Concept: Binding and Antibinding Regions

The chemical application of the concept of force was started by Berlin[4] in 1951. He was the first to distinguish between the use of words 'binding' and 'bonding' in the formation of a molecule. The word 'binding' relates to the forces acting on the nuclei and 'bonding' to the corresponding changes in energy. He gave a simple picture of chemical binding by dividing the three dimensional space of electrons into binding, antibinding and nonbinding regions.

Consider a diatomic molecule AB with R being the distance between A and B. The repulsive force between the nuclei with charges $+Z_A e$ on A and $+Z_B e$ on B is of magnitude $Z_A Z_B/R^2$ (in a.u.). Suppose, there is a bit of electronic charge of $-q$ at a point, say i (Fig. 11.1). This charge exerts an attractive force $-Z_A q/r_A^2$ on A in the direction **Ai** and an attractive force of $Z_B q/r_B^2$ on B in the direction **Bi**. Only the force exerted along AB axis has any effect on binding. We can break these forces into components parallel to the A–B axis (x-axis) and perpendicular to it, i.e., y-axis which is not useful. The net classical binding force on the nuclei due to charge $-q$ at a point (i) in the direction of the bond is therefore

$$f_{\text{binding}} = -q\left(\frac{Z_A \cos\theta_{Ai}}{r_{Ai}^2} - \frac{Z_B \cos\theta_{Bi}}{r_{Bi}^2}\right) \tag{11.23}$$

To obtain the total binding we have to sum Eq. (11.23) over the entire electron distribution. This is obtained by solving the Schrödinger equation for the system AB. Without solving the Schrödinger equation it is possible to get insight into the nature of the forces. If the point 'i' lies between A and B (i.e. $x_A < x_i < x_B$) we have $\theta_A < \pi/2$ and $\theta_B > \pi/2$, hence $\cos\theta_{Ai} > 0$ and $\cos\theta_{Bi} < 0$. For binding, f must be negative, when it means that electrons located near 'i' tend to pull the two nuclei toward each other. Thus the region between the two nuclei is a binding region.

If the point 'i' lies beyond the nuclei, say behind B, then $x_i > x_B$, $\cos \theta_{Ai}$ and $\cos \theta_{Bi}$ are both positive, and $r_{Bi}^2 < r_{Ai}^2$. Then $Z_B \cos \theta_{Bi}/r_{Bi}^2 > Z_A \cos \theta_{Ai}/r_{Ai}^2$ (for $Z_B = Z_A$) and according to Eq. (11.23) f binding becomes positive. Such a charge pulls A toward B and B away from A. Since the latter pull is greater when $Z_A = Z_B$, the two nuclei move away from each other. For equal nuclear charges, any negative charge on the x-axis to the right of B or the left of A is antibinding. The boundary surfaces that separate the binding region from the antibinding region are obtained by solving the equation

$$f_{\text{binding}} = -q\left[\frac{Z_A \cos \theta_{Ai}}{r_{Ai}^2} - \frac{Z_B \cos \theta_{Bi}}{r_{Bi}^2}\right] = 0 \tag{11.24}$$

These surfaces are called the nonbinding surfaces and are shown in Fig. 11.2 for a homonuclear diatomic. These boundary surfaces are hyperbolic contours. Any charge residing on these surfaces will not lead to any attraction or repulsion between the nuclei. On the other hand, removal of charge from the binding region results in an increase of bond length while charge removal from the antibinding region leads to a shortening of bond length.

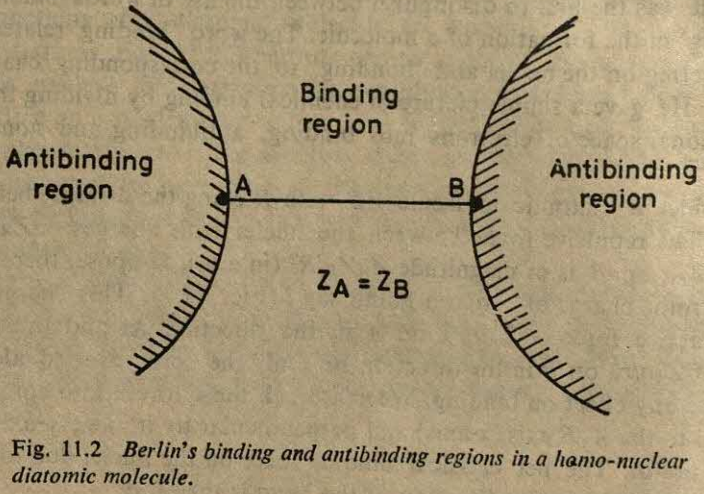

Fig. 11.2 *Berlin's binding and antibinding regions in a homo-nuclear diatomic molecule.*

Let us now consider the case where Z_A and Z_B are different. Consider HCl, where $Z_A = 17$, $Z_B = 1$ and Fig. 11.3. For the point 'i', $\cos \theta_{Ai}$ and $\cos \theta_{Bi}$ are positive. Since $Z_B = 1$, and even r_{Bi} is smaller than r_{Ai}, the first term of Eq. (11.23) dominates. So the force becomes binding. However, the region close to the H-nucleus will be antibinding. Therefore, for the electronic force to be binding along the bond, we have

$$\left(\frac{r_{Ai}}{r_{Bi}}\right)^2 < \frac{Z_A}{Z_B}$$

Using these arguments of Berlin one can show the binding (unshaded) and antibinding (shaded) regions (Fig. 11.3) for HCl.

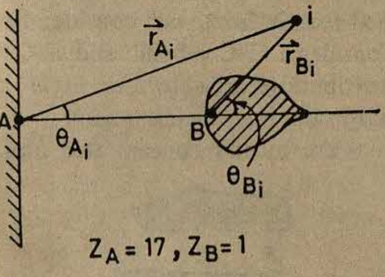

Fig. 11.3 *Binding (unshaded) and antibinding (shaded) regions of HCl.*

Since the net force on a nucleus, i.e. F_{Ax} (Eq. 11.20) which includes nuclear repulsion and electron-nuclear attraction is always zero for the equilibrium bond length, whether the bond is weak or strong, how can we then speak of a strong or a weak chemical bond from the force concept? We calculate the net force on the nucleus A, i.e. F_{Ax} along the bond-direction from Eq. (11.20) using the quantum mechanically calculated densities of AB. If this force is plotted as a function of R one obtains the curves shown schematically in Fig. 11.4 where F_{Ax} is zero when $R = \infty$ and $R = R_e$ (equilibrium bond length). The bond dissociation energy is given by the integral

$$\int_{\infty}^{R_e} F(R)\, dR$$

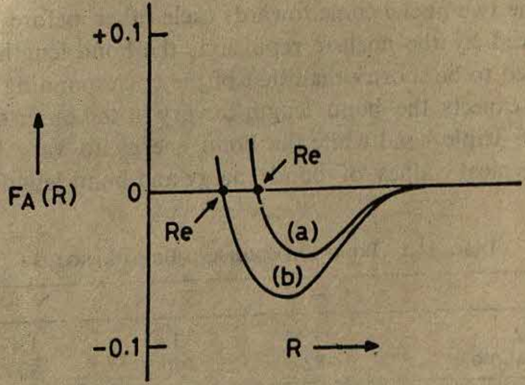

Fig. 11.4 *Schematic diagrams of the force curves of a strong and a weak bonds.*

The area encompassed by the curve (b) is greater than that by the curve (a) in Fig. 11.4. One can therefore say that the bond represented by the force curve (b) is stronger than the bond given by the force curve (a). Thus in a strong bond the net attractive force on a nucleus is larger than in a weak bond before their equilibrium bond lengths are reached in the bond-formation process.

The occurrence of the strong and weak bonds as well as that of short and long bonds in molecules can be understood readily from such consideration of the electrostatic force on a nucleus. Consider a C–C σ-bond and a C–C π-bond in a hydrocarbon. The electron distributions are shown in Fig. 11.5. In both the cases there are electron clouds in the internuclear region which is the binding region. In a σ-bond electrons are mostly concentrated along the internuclear axis and therefore they exert a stronger attractive force on each nucleus than in a π-bond where electrons are above and below the internuclear axis but nothing on this axis. This means that a C–C σ-bond is stronger than a C–C π-bond. Since the overall electron clouds are more in the binding region of a multiple bond than in a single bond, a nucleus in a multiple bond experiences a greater attractive force in the direction of the bond than in a single bond and hence a multiple bond is stronger than a single bond. Since stronger the attractive electronic force on a nucleus in a bond, closer the two nuclei come towards each other before the attractive force is balanced by the nuclear repulsion, the bond length of a multiple bond is expected to be shorter than that of the corresponding single bond. One therefore expects the bond length to vary in the order single bond > double bond > triple bond while the bond energy to vary in the reverse order. Some typical values of bond energy and bond lengths are given in Table 11.1.

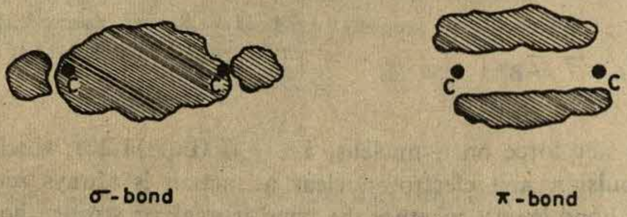

Fig. 11.5 *A schematic diagram of the electron distributions in a C-C σ-bond and a C-C π-bond.*

TABLE 11.1 BOND ENERGIES AND BOND LENGTHS

Bonds	C – C	C – N	N – N	C–O
Bond length (Å)	1.54	1.47	1.47	1.43
Bond energy (Kcal/mole)	82	70	38	84

Bonds	C = C	C = N	N = N	C = O
Bond length (Å)	1.33	1.22	1.25	1.23
Bond energy (Kcal/mole)	147	147	100	170

Bonds	C ≡ C	C ≡ N	N ≡ N	C ≡ O
Bond length (Å)	1.21	1.15	1.09	1.13
Bond energy (Kcal/mole)	194	210	226	262

(1 Kcal/mole = 4.184 KJ/mole)

11.5 Formation of Covalent and Ionic Bonds

Each MO makes a separate contribution to the density and thus total electronic force can be broken up into a sum of orbital contributions. One can write from Eq. (11.21)

$$\int \rho(r) \frac{\cos\theta_A}{r_A^2}\, d\tau = \sum_i^{\text{occ}} n_i \int \psi_i^2 \frac{\cos\theta_A}{r_A^2}\, d\tau \tag{11.25}$$

If we multiply both sides of Eq. (11.25) by R^2 we obtain the charge equivalent of the net electronic force on nucleus A. Thus, we define a quantity f_{iA} as

$$f_{iA} = R^2 n_i \int \psi_i^2 \frac{\cos\theta_A}{r_A^2}\, d\tau \tag{11.26}$$

Hence

$$R^2 \int \rho(r) \frac{\cos\theta_A}{r_A^2}\, d\tau = \sum_i^{\text{occ}} f_{iA} \tag{11.27}$$

One may now obtain from Eq. (11.20) the total force acting on A as[6]

$$F_A = \frac{Z_A}{R^2}\left[Z_B - \sum_i^{\text{occ}} f_{iA}\right] \tag{11.28}$$

When $R = \infty$ or $R = R_e$, i.e. the equilibrium value, $F_A = 0$ and $\sum_i^{\text{occ}} f_{iA} = Z_B$. In a homonuclear diatomic molecule each MO can be written as

$$\psi_i = \frac{1}{\sqrt{2 \pm 2S}} (\phi_A \pm \phi_B)$$

where S is the overlap between the atomic orbitals ϕ_A and ϕ_B. For large R, $S \to 0$,

$$\psi_i^2 = \tfrac{1}{2}[\phi_{iA}^2 + \phi_{iB}^2 \pm 2\phi_{iA}\phi_{iB}]$$

Since at large R, $\phi_A\phi_B \approx 0$, we have

$$\psi_i^2 = \tfrac{1}{2}[\phi_A^2 + \phi_B^2] \tag{11.29}$$

Since ϕ_{iA} and ϕ_{iB} are the centrosymmetric atomic orbitals on atoms A and B with which the MO ψ_i correlates for the separated atoms, the integrals

$$\int \phi_{iA}^2 \frac{\cos\theta_A}{r_A^2}\, d\tau = 0 \qquad \int \phi_{iB}^2 \frac{\cos\theta_A}{r_A^2}\, d\tau = \frac{1}{R^2} \text{ (in a u)}$$

because as $R \to \infty$, $r_A \to R$ and $\cos\theta_A \to 1$

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[6] This was introduced by Bader: See R.F.W. Bader and A.K. Chandra, *Can. J. Chem.*, 46, 953, (1968).

So from Eq. (11.26) and (11.29) one obtains

$$f_{iA}(R = \infty) = R^2 \frac{n_i}{2} \cdot \frac{1}{R^2} = \frac{n_i}{2} \tag{11.30}$$

For double occupation of a nondegenerate MO, the limiting value of f_{iA} is 1. For H_2, there is only one MO with two electrons and from Eq. (11.28) the force on a H-nucleus, A at large $R(R = \infty)$ is

$$F_A = \frac{1}{R^2}[1 - 1] = 0$$

If $f_{iA} > 1$ for $R < \infty$, the net force on the nucleus A is attractive, the MO ψ_i is then called the binding MO. If $f_{iA} < 1$ for $R < \infty$, the net force on the nucleus A is repulsive and the MO ψ_i may be then called the antibinding MO. If $f_{iA} \sim 1$, we have the nonbinding MO, as the density in such MO plays the same role in the molecule as in the separated atoms. This classification of the various MOs in terms of the electronic force which the orbital densities exert on the nuclei is complementary to the definitions of bonding and antibonding orbitals introduced by Mulliken[7]. The latter set of definitions is associated with the nodal characteristics and energies of MOs. They have been discussed in Chap. 7.

We shall consider the formation of the singlet and triplet states of H_2 from atoms in terms of the electronic force acting on a nucleus. In Fig. 11.6 is shown the variation of $f_{iA}(^1\Sigma_g^+)$ and $f_{iA}(^3\Sigma_u^+)$ for the singlet and triplet states with R. They are obtained from the ab initio wavefunctions given by Bowman et al. (1970)[8]. Figure 11.6 shows that at large R the singlet and triplet states of H_2 behave identically and such situation persists till $R \approx 7a_0$. For

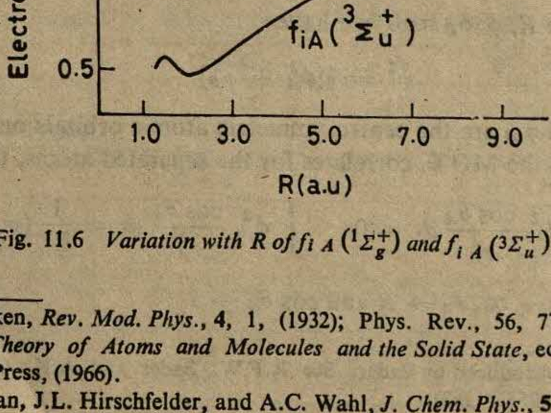

Fig. 11.6 *Variation with R of f_{iA} $(^1\Sigma_g^+)$ and f_{iA} $(^3\Sigma_u^+)$*

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[7] R.S. Mulliken, *Rev. Mod. Phys.*, 4, 1, (1932); Phys. Rev., 56, 778, (1939); and *Quantum Theory of Atoms and Molecules and the Solid State*, ed. P.O. Lowdin, Academic Press, (1966).

J.D. Bowman, J.L. Hirschfelder, and A.C. Wahl, *J. Chem. Phys.*, 53, 2743, (1970).

$R < 7a_0$, the density in the singlet state becomes more and more binding corresponding to a net force of attraction and the eventual formation of a stable bond. While in the triplet state the density becomes more and more antibinding corresponding to a net force of repulsion. The variation of f_{iA} with R further shows that in the formation of the stable H_2 $(^1\Sigma_g^+)$ molecule, f_{iA} becomes again equal to unity at $R = R_e(1.4a_0)$ and the electrostatic equilibrium is attained.

It is possible to partition the charge density ρ_i in each MO of a diatomic molecule AB as

$$\rho_i = \rho_{iA} + \rho_{iB} + \rho_{iD}$$

where ρ_{iA} and ρ_{iB} are the atomic populations and ρ_{iD} is the component of density which is delocalised over the molecule as a result of atomic interaction. Therefore f_{iA} can be split into three parts as

$$f_{iA} = f_{iA}^{\rho A} + f_{iA}^{\rho B} + f_{iA}^{\rho D}$$

where $f_{iA}^{\rho A}$ is called the charge-equivalent of the force on nucleus A by the atomic density on A. If this density is undeformed from that of atoms it exerts no force on A. So at $R = \infty$, this force becomes zero. However, deformation of atomic distribution for $R < \infty$ as described by $s - p$ or $p - d$ mixing results in a force on A.

$f_{iA}^{\rho B}$ is called the charge equivalent of the force on A by the density centered on B. It is a measure of shielding of nucleus B from A by electrons on B. When $R = \infty$, $f_{iA}^{\rho B} = f_{iA} = 1$ for double occupation of the i^{th} MO, (see Eq. 11.30). For $R < \infty$ $f_{iA}^{\rho B}$ is generally less than unity resulting in unshielded nucleus, because the nucleus A penetrates into the spherical charge density on the nucleus B.

$f_{iA}^{\rho D}$ is the charge equivalent of the force on either nucleus by the overlap density. If the atomic interaction results in the transfer of density into the overlap region this density provides an attractive force on both nuclei leading to binding. However for large $R(R = \infty)$, $f_{iA}^{\rho D} = 0$.

In Fig. 11.7 are shown the variations of $f_{iA}^{\rho D}$ with R for the $(^1\Sigma_g^+)$ and $(^3\Sigma_u^+)$ states of H_2. Results show that $f_{iA}^{\rho D}$ increases in the singlet state as R is decreased implying a transfer of density in the binding region until it reaches a maximum. On further decrease of R, the charge density is transferred behind the nuclei, causing a decrease of $f_{iA}^{\rho D}$. On the other hand, in the triplet state, the variation of $f_{iA}^{\rho D}$ with R implies a charge-transfer from the binding region to the antibinding region (i.e. the region behind the nuclei). Such density can cause the nuclei to move away from one another. This effect in the triplet state of H_2 arises from the fact that the two electrons with their parallel spins cannot simultaneously occupy the same region of space.

The variation of $f_{iA}^{\rho B}$ with R are also shown in Fig. 11.7 for the singlet and triplet states. As expected, in the singlet state the nucleus A penetrates into the charge cloud of the other atom causing a decrease of $f_{iA}^{\rho B}(^1\Sigma_g^+)$

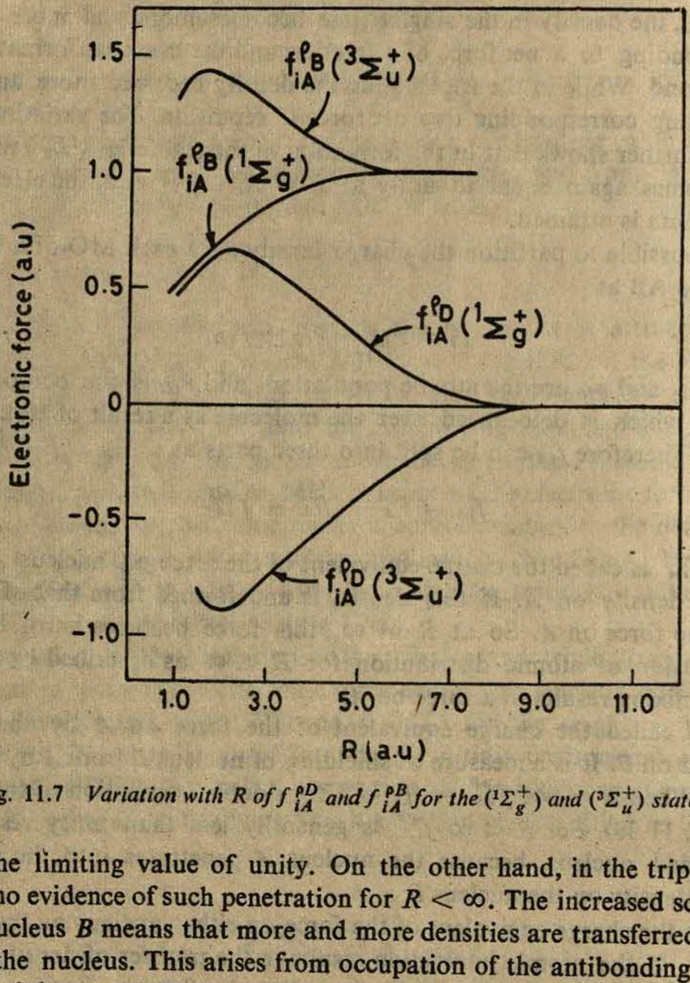

Fig. 11.7 *Variation with R of* $f_{iA}^{\rho D}$ *and* $f_{iA}^{\rho B}$ *for the* ($^1\Sigma_g^+$) *and* ($^3\Sigma_u^+$) *states.*

below the limiting value of unity. On the other hand, in the triplet state there is no evidence of such penetration for $R < \infty$. The increased screening of the nucleus *B* means that more and more densities are transferred to the site of the nucleus. This arises from occupation of the antibonding σ_u MO in the triplet state. The atomic population in a σ_u MO is proportional to $1/1-S$. As *R* is decreased, *S* tends to approach unity and thereby causes a large increase of density on the nucleus. This increase of the screening term beyond the limiting value implies an attraction between the atoms in the triplet state. However, this increase is small and more than offset by the highly repulsive overlap term.

The variation of the atomic term $f_{iA}^{\rho A}$ with *R* is shown in Fig. 11.8 for both the singlet and triplet states. At large *R*, say $R \geqslant 5a_0$, the overlap is negligible. In the singlet state the atomic density is polarised towards the internuclear region resulting in an attractive force on each nucleus. In the triplet state the electron cloud around each nucleus is polarised behind the nucleus resulting in repulsion. For both states $f_{iA}^{\rho A}$ must converge to zero at $R = 0$, because in the united atom the electron cloud becomes again centrosymmetric.

These results derived from electrostatic forces can be readily visualised through the variation of the three-dimensional density difference with *R*. For

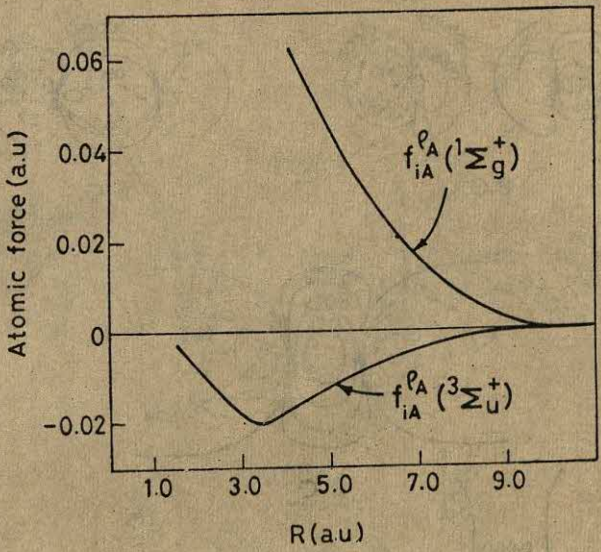

Fig. 11.8 *Variation of the atomic term, i.e.* $f_{iA}^{\rho A}$ *with R.*

a diatomic molecule the density difference $\Delta\rho$ is defined as

$$\Delta\rho(\hat{\mathbf{r}}) = \rho_{\text{mol}}(\hat{\mathbf{r}}) - \rho_{\text{atoms}}(\hat{\mathbf{r}})$$

where $\rho_{\text{mol}}(\hat{\mathbf{r}})$ is the molecular electron density at a point $\hat{\mathbf{r}}$ in space and $\rho_{\text{atoms}}(\hat{\mathbf{r}})$ is that obtained by the overlap of the unperturbed atomic densities. The atomic distribution $\rho_{\text{atoms}}(\hat{\mathbf{r}})$ is the sum of contributions from each atom, the nucleus of which occupies a position identical to that found in the molecular system. The contours of this difference density, when plotted as functions of R, would reveal pictorially the reorganisation of charge which accompanies the formation of a stable bond in the singlet state and an unstable bond in the triplet state. They are shown in Figs. (11.9) and (11.10) for the singlet and triplet states, respectively.

Figure (11.9) reveals that when $R = 8\ a_0$ the overlap is negligible but each atomic densities are polarised towards the other atom. The result of this polarisation is that each nucleus experiences a binding force by its own distorted density towards the other atom. This is the electrostatic description of Van der Waal's force as foreseen by Feynman^2. It is not the interaction of the two created dipoles at the two centres that leads to Van der Waal's force.

When R is decreased the overlap of the atomic distributions become appreciable and an increasing amount of charge is transferred from the antibinding to the binding region in the singlet state. But, a surprising fact also emerges from Fig. 11.9. At the equilibrium configuration ($R = 1.4\ a_0$) there is also a charge build-up behind the nuclei. And at distances less than

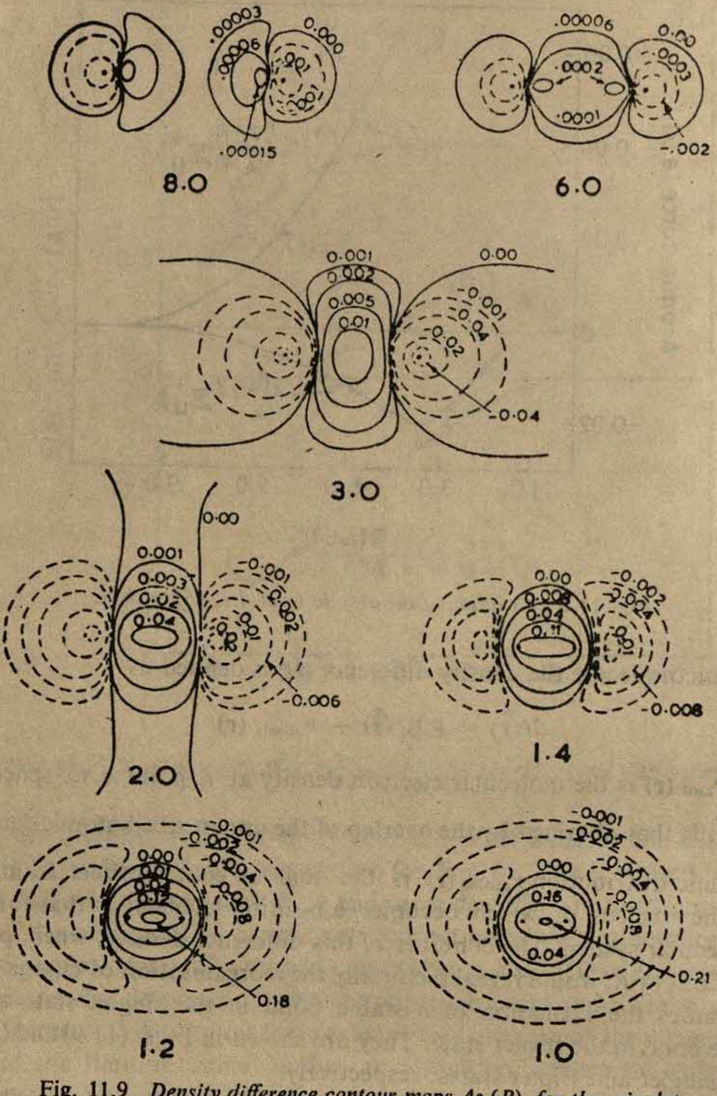

Fig. 11.9 *Density difference contour maps Δρ (R) for the singlet H_2 at the indicated values of R (a.u). The maps of R =8.0 a.u and 6.0 a.u are drawn to half the scale of others (with permission of the National Research Council of Canada, from R.F.W. Bader and A.K. Chandra, Canad. J Chem.,* **46**, *953-966, 1968).*

1.4 a_0 this accumulation of charge in the antibinding region increases. This is responsible for the steep repulsive part of the potential energy curve.

Figure (11.10) shows how the charge redistribution takes place in the triplet state. These diagrams are the approximate opposites of the Δρ-maps for the singlet state of H_2. Here, the densities increase in the region behind the nuclei as well as in the vicinity around each nucleus at the expense of densities in the internuclear region as R is decreased. At $R = 1.4\ a_0$

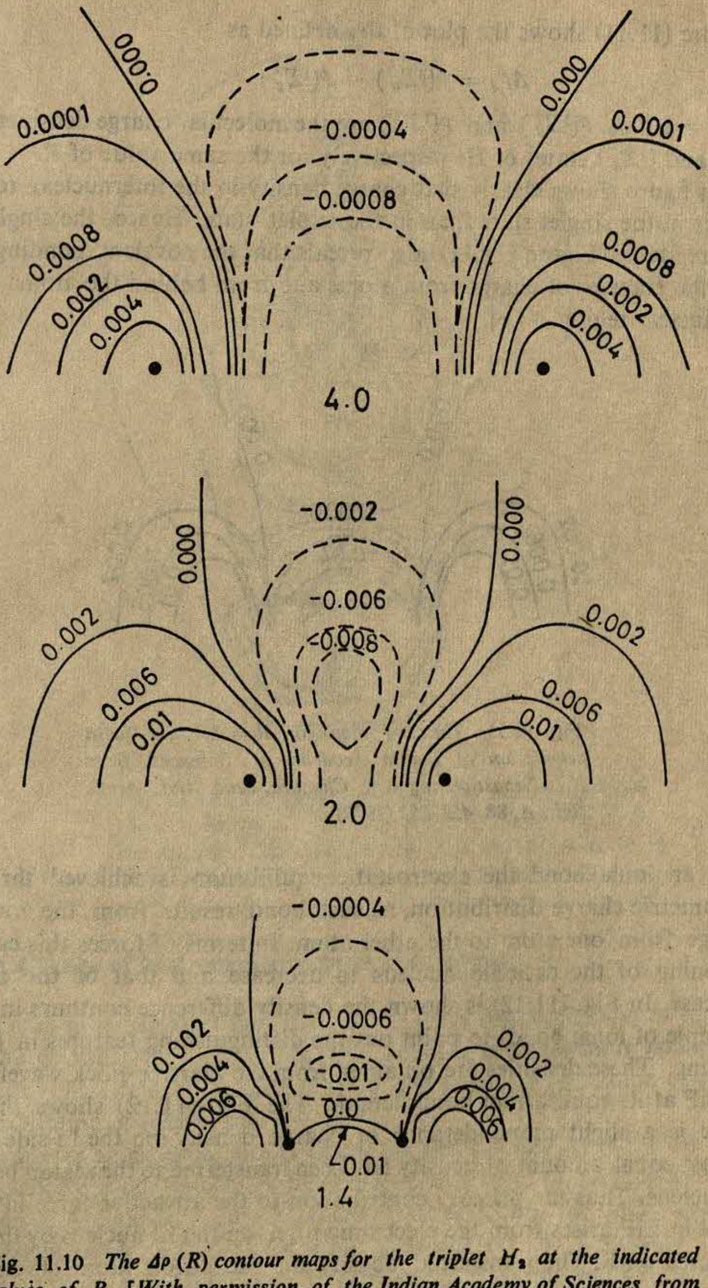

Fig. 11.10 *The Δρ (R) contour maps for the triplet H_2 at the indicated values of R.* [*With permission of the Indian Academy of Sciences from K.L. Sebastian and A.K. Chandra, Proc. Ind. Acad. Sci. A,* **88**, *445-552, (1979)*]. *The lower half is the mirror image of the upper half due to symmetry.*

Fig. (11.10) shows that there is an indication of slight increase of density in the internuclear region. But this increase is not large enough to offset nuclear repulsion, and the triplet state is unstable.

Figure (11.11) shows the plot of $\Delta\rho_e$ defined as

$$\Delta\rho_e = \rho(^3\Sigma_u^+) - \rho(^1\Sigma_g^+)$$

for $R = 1.4\ a_0$. $\rho(^3\Sigma_u^+)$ and $\rho(^1\Sigma_g^+)$ are the molecular charge densities of the $(^3\Sigma_u^+)$ and $(^1\Sigma_g^+)$ states of H_2 respectively for the same value of R.

This figure shows clearly that charge density in the internuclear region is greater in the singlet state than in the triplet state. Hence, the singlet state is more stable. Figure (11.11) also reveals that the covalent bonding arises from the transfer of charge from atoms and from behind the atoms to the internuclear region.

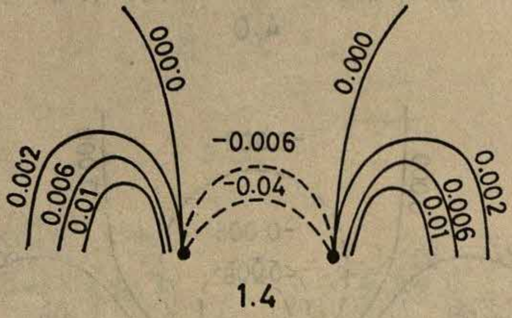

Fig. 11.11 *The $\Delta\rho_e$ map for $R = 1.4$ a.u* [*with permission of Indian Academy of Sciences from K.L. Sebastian and A.K. Chandra, Proc. Ind. Acad. Sci., A,* **88**, *452-552 (1979)*].

In an ionic bond the electrostatic equilibrium is achieved through an asymmetric charge distribution, as such bond results from the transfer of charge from one atom to the other atom. In terms of forces this causes the screening of the cationic nucleus to decrease and that of the anion to increase. In Fig. (11.12) is shown the density difference contours in LiF (an example of ionic bond) to point out the distinguishing features in chemical binding. These densities are obtained from the Hartree-Fock wavefunctions of LiF at its equilibrium bond length. The Fig. (11.12) shows that while there is a slight preponderance of charge density on the Li-side of F, an almost equal amount of density has been transferred to the region behind the F-nucleus. Thus the primary contribution to the attractive force in the ionic bond in LiF arises from the electronic force on the Li nucleus by the density centered on F. The transferred density on the anion atom (F in LiF) is almost symmetrically placed around it rather than between the nuclei. In a covalent bond the primary contribution to the attractive force that binds the two nuclei arises from the overlap density.

These revelations do neither contradict the earlier concept of chemical bonding nor lead to any exciting discovery. But this analysis certainly provides a deeper insight into the nature of the process and gives chemists enough confidence to employ this classical concept in chemistry.

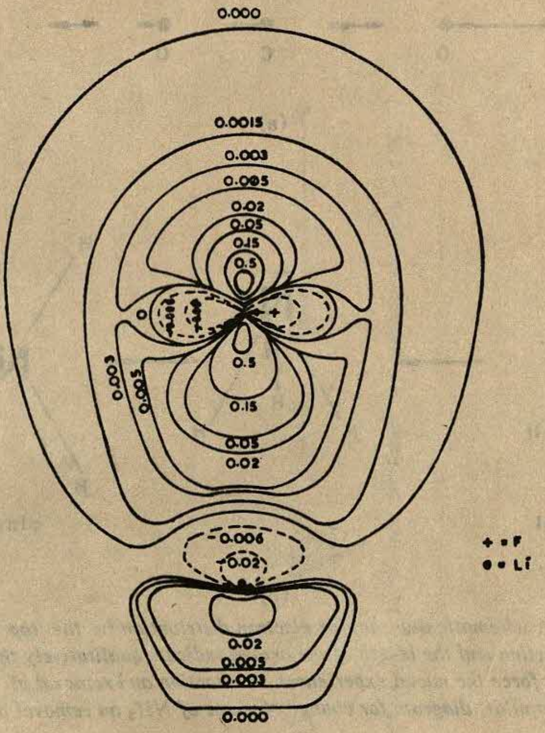

Fig. 11.12 *The molecular minus the atomic densities for the density distributions in LiF [with permission of the American Chemical Society, from R.F.W. Bader and W.H. Henneker, J. Am. Chem. Soc., 87, 3063, (1965)].*

11.6 Change of Molecular Structures and Shapes

The gain in physical insight that results from the application of the concept of the electrostatic force to chemical bonding becomes more apparent when we turn our attention to the change of the structure and shape of molecules on excitation or ionisation.

Consider an example of CO where the electron density in the top occupied molecular orbital lies behind the carbon nucleus and remote from the oxygen nucleus. An electron in such a cloud attracts both the nuclei as shown by the arrow heads in Fig. 11.13(a) but the force on the C-nucleus is greater than that on the O-nucleus. If this electron is removed by ionisation the previous equilibrium configuration will be modified by a net force pushing the C-nucleus toward the O-nucleus until the net electrostatic force becomes zero when we have a new equilibrium configuration. The bond length in CO^+ should drop. This is precisely what is found. The observed C–O distance in CO drops from 1.13 Å to 1-11 Å in CO^+. Similarly, if one of the lone pair electrons is removed from ammonia, the pyramidal shape of

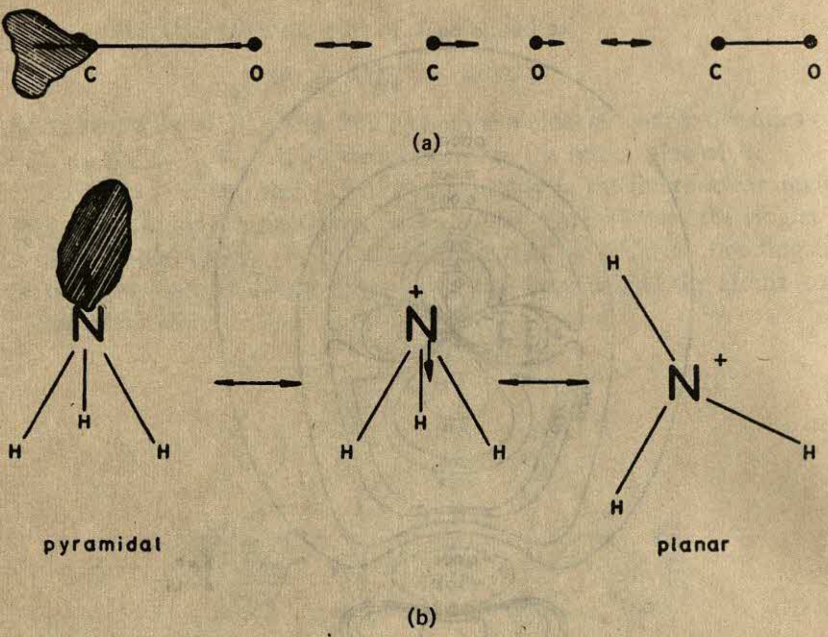

Fig. 11.13 (*a*) *A schematic diagram for electron distribution in the top occupied MO of CO. The direction and the length of the arrows indicate qualitatively the direction and magnitude of the force the nuclei experiences on retention and removal of the lone pair density,* (*b*) *A similar diagram for change of shape of NH_3 on removal of the lone pair density.*

ammonia becomes modified by a net force which pushes the N-nucleus toward the plane containing the three H-nuclei (Fig. 11.13b) causing NH_3^+ to assume a planar structure.

One can extend this kind of argument to predict the change of molecular shapes on excitation. Consider a non-linear triatomic molecule (Fig. 11.14). On excitation, suppose, electrons are transferred to the different regions as shown in Fig. (11.14). Such a change in electron distributions will now induce the nuclear movement as shown by the arrow heads in Fig. (11.14) until these forces become zero and the molecule becomes linear. Thus, the ground and excited states have the different nuclear shapes. During such movement of nuclei the orbitals of the central atom are likely to be polarised. This is important so far as the force concept is concerned. When we have a pure p-orbital as the non-bonding orbital on an atom with a pair of electrons in it, they exert equal force on the nucleus in the opposite directions as shown by the arrows in Fig. (11.15). On the other hand, if the *p*-orbital is mixed with an *s*-orbital to form any kind of the *s-p* hybridisation, the electron distribution becomes more on one side than on the other resulting in a net force on the nucleus in the direction of the largest density. Nakatsuji[9] called this force the driving force (or the atomic dipole force) which causes the molecule to change its shape.

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[9] H. Nakatsuji, *J. Am. Chem. Soc.*, **95**, 345, 354, (1973)

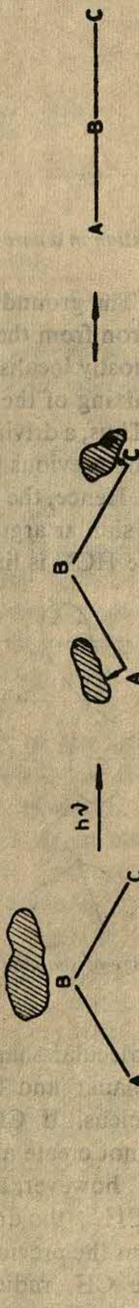
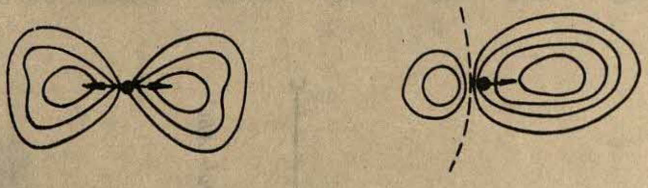


Fig. 11.14 *A schematic diagram showing change of shape on electron excitation in a triatomic molecule ABC.*



p-orbital s-p orbital

Fig. 11.15 *Electron distribution in a pure p- and a hybrid sp-orbitals.*

Let us now see how it works. The ground state of formaldehyde is planar. In its lowest n-π^* state, an electron from the lone pair orbital of the O-atom goes to the π^*-orbital which is mostly localised on the C-atom. The bending of the molecule will cause the mixing of the pure $2p_\pi$ orbital of the C-atom with some amount of $2s$-orbital. Thus, a driving force is rapidly generated and pulls the C-nucleus away from the previous plane (Fig. 11.16) until the net force on the C-nucleus vanishes. Hence, the equilibrium structure of CH_2O in its $n\pi^*$ state is non-planar. A similar argument predicts the bent structure of HCN in its excited state while HCN is linear in its ground state.

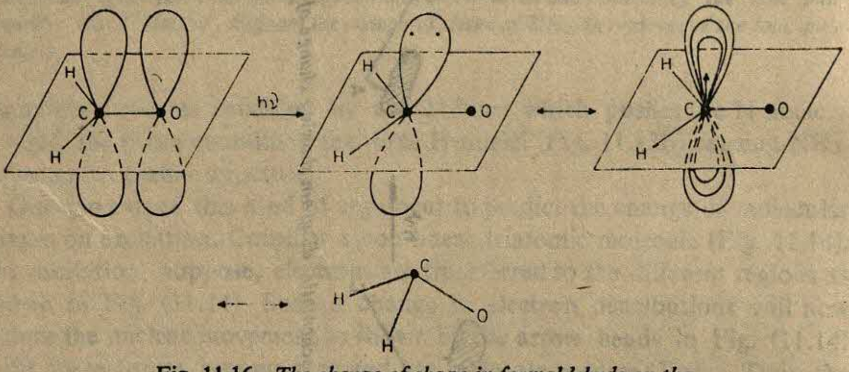


Fig. 11.16 *The change of shape in formaldehyde on the $n \to \pi^*$ excitation.*

We shall now examine the molecular shapes of the CH_3^+, CH_3^0 and CH_3^- systems. The CH_3^+ system is planar and has the D_{3h} symmetry with an empty $2p$-orbital on the C-nucleus. If CH_3^+ is bent, the mixing of this $2p$-orbital with a $2s$-orbital will not create any driving force as long as such hybrid orbital remains empty. If, however, a pair of electrons is assumed to occupy such orbital as in CH_3^-, the driving force will rapidly develop and pull the C-nucleus away from the previous plane (Fig. 11.17), and make it pyramidal as in NH_3. In the CH_3 radical, magnitude of such driving force is not sufficient to cause any large deviation from the planar configuration. However, the CF_3^0 radical is nonplanar because each F-atom is π-donating to the half filled nonbonding orbital on carbon.

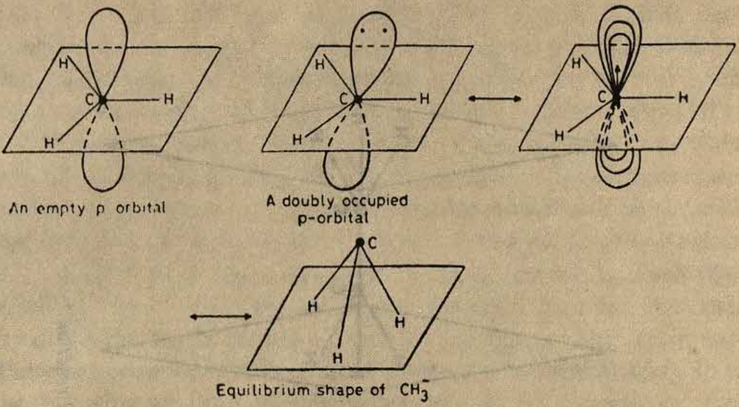


Fig. 11.17 *An empty p-orbital in CH_3^+ and a doubly occupied p-orbital in CH_3^- causing a difference in their molecular shapes.*

The change of shape of molecules and the structure of the product formed during chemical reaction can also be understood from the consideration of the electrostatic force. Though methyl radical in its ground state is planar, during reaction between two such radicals leading to the formation of ethane, the structure of each methyl fragment changes (Fig. 11.18). When a new chemical bond is formed between two methyl radicals the density from the backlobe of each *p*-orbital on the C-nucleus of each CH_3^0 radical migrates into the inter-nuclear region, as it happens during the formation of H_2. This build-up of density in the internuclear region, mostly on the internuclear axis, will draw the two C-nuclei towards each other and away from the planes containing the H-nuclei. Thus, each methyl fragment assumes the non-planar structure as in ethane. A similar phenomenon is noticed in the acid-base reaction between BF_3 and NH_3. In the adduct, BF_3-NH_3, the FBF angle is 111° while in free BF_3 it is 120°. It should be noted that the redistribution of electrons and the change of hybridisation during reaction are different manifestations of the same origin.

Deb[10] used a postulate that the highest occupied molecular orbital (HOMO) determines the shape of a molecule. With this postulate he was able to predict the change of shape of many molecules on excitation and ionisation. The geometry predictions made on the basis of the HOMO-postulate are remarkably consistent with known geometries. The question arises; why is the HOMO so important for molecular geometry? Among the MOs, electrons in the HOMO are most loosely bound. The density due to other occupied MOs tends to follow the nuclear motion and has therefore less influence on molecular shape. In HOMO, electrons are loosely bound with the nuclei. So when the nuclei move electrons do not follow the nuclear

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[10] B.M. Deb, *J. Am. Chem. Soc.*, **96**, 2030, (1974).

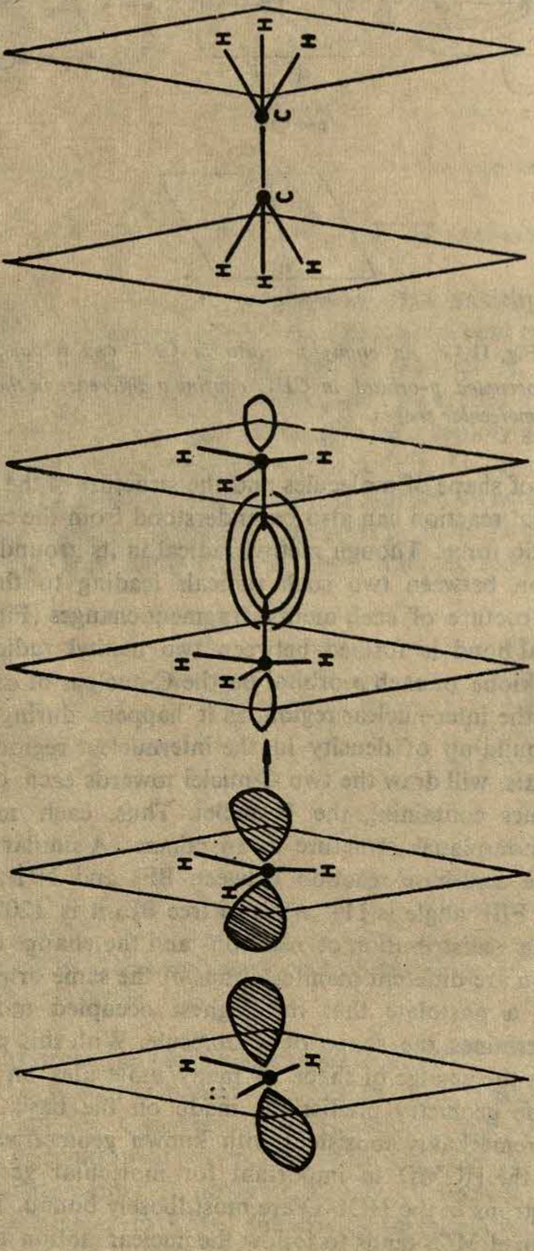

Fig. 11.18 *The change of shape in methyl radicals on chemical reaction.*

motion but relax. This incomplete following of the HOMO-electrons is responsible for the change of shape and the success of the HOMO postulate.

One can apply the Hellmann-Feynman theorem to the problem of configurational instability in molecules or the static Jahn-Teller (J-T) effect[11]. The J-T theorem may be stated as follows: a poly-atomic molecular configuration in which the electronic state is orbitally (or spin) degenerate cannot be stable except when (a) the configuration involved is linear and (b) the system contains an odd number of electrons. The polyatomic molecule will tend to distort to a lower symmetry so as to remove as much degeneracy as possible. The J-T theorem provides a powerful tool for discussing geometry of distortions in certain inorganic complexes, although in such cases the theorem seems to have been used somewhat indiscriminately in the past. In the following we shall consider very briefly the J-T distortion in the ground state of VCl_4.

VCl_4 differs from the hypothetical VCl_4^+, a tetrahedral molecule, only in the presence of one electron. The two-fold orbital degeneracy in the ground state of VCl_4 arises because this electron may be regarded as occupying either a non-bonding d_{z^2} or a non-bonding $d^2_{x^2-y^2}$ orbital of the vanadium atom (Fig. 11.19) both orbitals having the same energy. A J-T distortion will result because of the following considerations: In the equilibrium nuclear configurations of VCl_4^+ (regular tetrahedron) there is no net force on any chlorine nucleus. Now, when the non-bonding electron is introduced in the VCl_4 framework every chlorine nucleus will experience an extra force and, therefore, will move to a new equilibrium position. If we assume that the electronic distribution in VCl_4^+ remains unaltered in VCl_4, then this extra force on each chlorine nucleus is just the electron-nuclear attraction due to the extra electron. The new equilibrium positions will obviously depend upon whether the extra electron goes into a d_{z^2}or a $d_{x^2-y^2}$ orbital.

In view of the above considerations, a close look at Fig. (11.19) leads to the following logical conclusions: (i) the extra electron will cause an equal decrease in each V-Cl bond length (relative to VCl_4^+); but, this by itself will not reduce the molecular symmetry; (ii) the J-T distortion, viz. a flattening or an elongation of the tetrahedron, will occur only in the plane defined by the metal z-axis and the relevant V-Cl bond; (iii) if the extra electron is in the d_z^2 orbital [Fig. 11.19(a)] then the circumscribing cube would be elongated in the z-direction (obviously, there will be three such equivalent distorted forms since there is no unique choice for the z-direction); on the other hand, if the electron goes into the $d_{x^2-y^2}$ orbital [Fig. 11.19(b)] the cube will be flattened; and (iv) since the two orbitals, d_{z^2} and $d_{x^2-y^2}$, lead to opposite types of distortion the extra electron is more likely to be in either of them than in a linear combination of the two; clearly, the latter situation would result in less stabilisation energy due to a J-T distortion. Numerical calculations of Coulson and Deb[12], however, do not indicate any preference of

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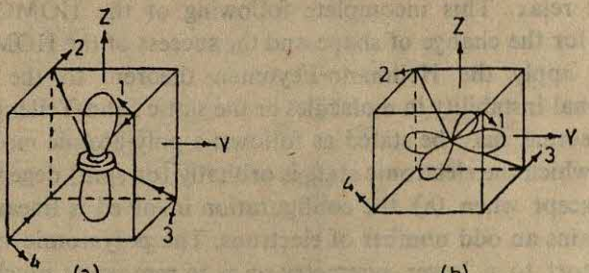
[11] H.A. Jahn and E.D. Teller, *Proc. Roy. Soc.*, **161A**, 220, (1937).

[12] C.A. Coulson and B.M. Deb, *Molec. Phys.*, **16**, 545, (1969).



(a) (b)

Fig. 11.19 *The static Jahn-Teller effect in VCl_4 using (a) metal d_{z^2} atomic orbital and (b) metal $d_{x^2-y^2}$ atomic orbital. The arrows on ligand atoms indicate the directions of distortion. Arrows 1, 2, 3 and 4 lie in the planes defined by the metal z-axis and the relevant V–Cl bonds.*

the extra electron for one orbital or the other. This means that, according to the simple qualitative approach outlined here, both the flattened and elongated tetrahedra are equally likely for VCl_4. This conclusion agrees very well with recent electron spin resonance experiments.

11.7 An Examination of the Gillespie-Nyholm Model of the Molecular Structure

In 1950, Lennard-Jones and Pople[13] pointed out that water and ammonia could be described in terms of sp^3-hybrid orbitals on the central atom, which are occupied by two bonding and two lone pairs of electrons in water and three bonding and one lone pair in ammonia. Gillespie and Nyholm[14] have shown that these ideas can be extended to account for the general shapes and bond angles of most inorganic molecules. They pointed out that the arrangement of electron-pairs in a valence shell of the central atom in a molecule could be regarded as arising from the mutual repulsions between the electron-pairs. These repulsions are not coulombic but arise from operation of the Pauli exclusion principle. The physical basis of the Gillespie and Nyholm model is that the Pauli principle forces electron pairs to occupy different regions of space. When some of the valence electron pairs are non-bonding whilst others are bonding as in H_2O, then the lack of equivalence is reflected in a distortion of the molecular structure. Gillespie and Nyholm assumed that the inter-electron pair repulsions vary in the order; non-bonding—non-bonding > non-bonding—bonding > bonding—bonding. Thus, in the series, CH_4, NH_3 and H_2O the successive replacement of bonding pairs by lone pairs causes the bond angle to decrease from 109.5° in CH_4 to 107.2° in NH_3 and to 104.5° in H_2O.

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[13] J.E. Lennard Jones and J.A. Pople, *Proc. Roy. Soc. A*, **202**, 166, (1950).

[14] R J. Gillespie and R.S. Nyholm, *Quart. Revs*., **339**, (1957).

Bader and Preston[15] have critically examined this electron-pair repulsion concept. These authors demonstrate that interpretations of such repulsions in terms of colliding orbitals in real space is misleading. Also, by considering the molecules like H_2O and NH_3 they have shown that the shifts in the electron density arising from the Pauli principle do not lead to a decrease in the tetrahedral bond angle in H_2O and NH_3 and furthermore, the interactions between the bonding orbitals are larger than those involving lone-pair orbitals. Therefore, the basis of the Gillespie-Nyholm model becomes doubtful. Bill and Snow[16] have also examined the electron-pair repulsion concept and concluded that the Pauli principle is not really responsible for the geometry change in molecules. Hall[17] has made another assessment of the role of the Pauli repulsion in determining the geometry of molecules. He examined the energy of water as function of the bond angle using the Hartree-product functions and the Hartree-Fock functions. The strong similarity between these two results, so far as the shape of the molecule is concerned, strongly suggest that the exchange terms are not critical in determining the gross geometry of molecules, as long as the orbitals are orthogonal. When the orthogonality restrictions are removed, it means a severe violation of the Pauli principle, the bond angle in water decreases to 45°. This behaviour indicates that the Pauli repulsions in H_2O are between bond pairs and not between lone pairs or between a lone-pair and a bond-pair.

The lack of proper theoretical basis of the electron-pair repulsion concept manifests itself in its failure to explain the change of bond length when the bond pair is replaced by the lone pair. For example, NH_4^+ is a regular tetrahedron with four equivalent N-H bonds. If an N-H bond is replaced by a lone-pair of electrons as in NH_3, the N-nucleus experiences a driving force in the direction of lone-pair until the net force on N is zero. This will cause the N-atom to move in the direction of the arrow (Fig. 11.20) while the three H-atoms remain approximately in the same positions as they were in NH_4^+. Thus, the N-H bond length increases and the H-N-H bond angle decreases. Similarly, if, in CH_4 which is a regular tetrahedron a C-H bond is replaced by a vacant orbital to form CH_3^+, the carbon nucleus will experience a force to cause it to move towards the plane containing the three hydrogen nuclei until the net force on carbon is zero. This will cause the equilibrium bond angle H–C–H to increase and the C–H bond length to decrease. In Table 11.2 are listed values of bond angles and bond lengths of a few molecules to demonstrate the possibility of determining the equilibrium geometry of polyatomic molecules from the classical concept of electrostatic force. It is to be noted that although the electron-pair repulsion theory of Gillespie and Nyholm explains the change of bond angles when

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[15] R.F.W. Bader and H.J.T. Preston, *Canad. J. Chem.*, **43**, 1131, (1966).

[16] J. Bills and R.L. Snow, *J. Am. Chem. Soc.*, **97**, 6340, (1975).

[17] M.B. Hall, *J. Am. Chem. Soc.*, **100**, 6333, (1978).

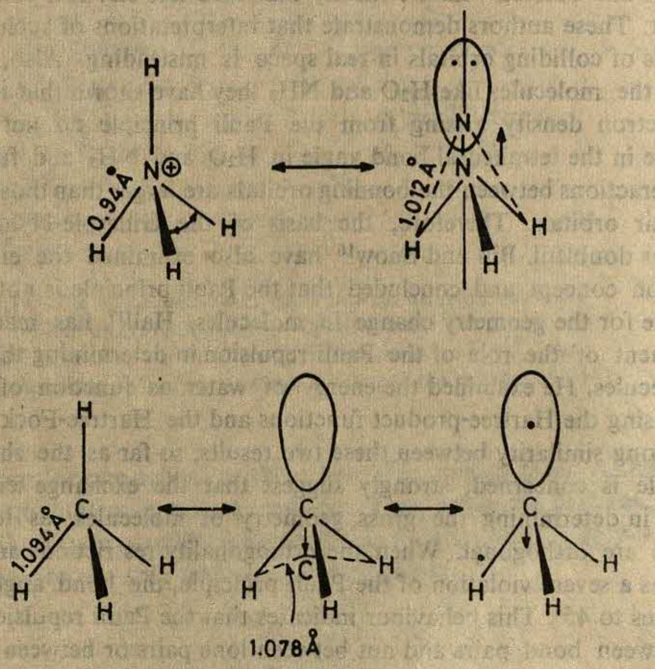


Fig. 11.20 *Change of bond angle and bond length when a bond-pair is replaced by a lone-pair. The size of the arrow is proportional to the magnitude of the displacement of the central atom.*

TABLE 11.2 *Bond angles and bond lengths of a few molecules*

Molecules	Bond angles (θ) (degrees)	Bond lengths Å
NH_4^+	109.5	0.94 ± 0.03
NH_3	107.0	1.012
PH_4^+	109.5	1.420
PH_3	93.3	1.437
CH_4	109.5	1.094
CH_3^+ / CH_3	120.0	1.078
BH_3	120.0	1.220
BH_2^-	102.0	1.243

the bond-pair is replaced by the lone-pair or vice-versa it does not explain the change of bond length which is small but significant.

A systematic analysis of electronic distributions in terms of the electrostatic force they exert on a nucleus in a molecule thus becomes a powerful tool for gaining insight in numerous chemical problems. However, it is important to emphasise that this approach is neither a contradiction of, nor a substitute for, calculations made by the traditional methods. Although the traditional approach generally provides more accurate numbers, the quantitative consequence of the force approach can be improved with increasing accuracy of the wavefunctions without affecting the underlying conceptual simplicity and visuality. Besides, the force approach seems to have a high pedagogic value in chemistry. Hence, it deserves wider use and further development.

PROBLEMS

1. Consider a hydrogen bond of an acid HA with a base *B* (i.e. *A–H. . . . B*). If we assume that the electronic charges centered on *A* and *B* are spherical, show that, on formation of a stable hydrogen bond, the bond length in *H–A* is increased over the free acid value.
2. Find from the force concept that a non-planar molecule DA_4 with four equivalent *D–A* bonds is a regular tetrahedron. If, however, one *D–A* bond is broken and DA_3^+ is formed without any lone-pair of electrons, the molecule becomes planar.
3. According to a semiempirical calculation the lone-pair orbital on nitrogen in ammonia is given by $\psi_N \approx C_1(2s_N) + C_2(2p_N)$ where $2C_1C_2 = 1.063$ compared with 0.866 for sp^3 hybrid orbital. Find the atomic dipole force on the nitrogen nucleus. Use the Slater 2*s*– and 2*p*–atomic orbitals of nitrogen.
4. Calculate the net force on a helium nucleus in He_2 using the simple $1\,\sigma_g$– and $1\,\sigma_u$– MOs made up of the Slater 1*s*-atomic orbitals ($\alpha = 1.69$), when the internuclear separation is in the range of $4.0 \sim 8.0$ a.u.

Answers to Problems

Chapter 1

1. $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_eE}} = \frac{6.6\times10^{-27}\times10^{8}}{(2\times9.1\times10^{-28}\times2.5\times1.6\times10^{-12})^{1/2}}(\text{A})$

   $= 7.734\ \text{Å}$

2. $E = \frac{hc}{\lambda} = \frac{6.6\times10^{-27}\times3\times10^{10}}{7.5\times10^{3}\times10^{-8}}$ erg/molecule

   $= \frac{6.6\times3.0}{7.5\times1.6}\ \text{eV} = 1.65\ \text{eV}$

3. Expressing the exponential factor in terms of sine and cosine functions, we obtain

   $\exp\left(+\frac{2\pi i}{\lambda}x\right) = \cos\frac{2\pi}{\lambda}x + i\sin\frac{2\pi}{\lambda}x$

   When $\Delta x = \pm\lambda$,

   $\frac{2\pi}{\lambda}\Delta x = \pm2\pi$

   Thus, the argument of the sine and cosine terms changes by 2π. As each term goes through one cycle, ψ does also.
4. 6.9 keV.

Chapter 2

1. This can be proved in a way analogous to the proof for hermitian operators. See Theorem in Sec. 2.7.1.
2. Consider the equation

$$\frac{h}{2\pi i}\frac{\partial}{\partial x}\psi = \lambda\cdot\psi$$

$$\frac{\partial\psi}{\partial x} = \frac{2\pi i}{h}\lambda\cdot\psi$$

$$\psi = \exp\left(\frac{2\pi i}{h}\lambda\right)x$$

   Let $k = \frac{2\pi}{h}\lambda$, then $\exp(ikx)$ is the eigenfunction with eigenvalue $kh/2\pi$. Since there is no restriction in the value of k, the eigenvalue of $\frac{h}{2\pi i}\cdot\frac{\partial}{\partial x}$ can form a continuous spectrum.

3. $\hat{A}\psi = a\psi$

Hence $\hat{A}^2\psi = \hat{A}(a\psi) = a(\hat{A}\psi) = a^2\psi$

Similarly, $\hat{A}^n\psi = \hat{A}\hat{A}\hat{A} \ldots \hat{A}\psi = a^n\psi$

Since
$$\exp(A) = 1 + A + A^2/2! + A^3/3! + \ldots$$
$$= \sum_n \frac{1}{n!}A^n$$

We have
$$\widehat{(\exp A)}\,\psi = \left(\Sigma\, \frac{1}{n!}\hat{A}^n\right)\psi = \left(\sum_n \frac{1}{n!}a^n\right)\psi$$
$$= (\exp a)\cdot\psi$$

4. $x^n p_x\psi = x^n \dfrac{h}{2\pi i}\dfrac{\partial\psi}{\partial x}$

$$p_x\, x^n\,\psi = \frac{h}{2\pi i}\frac{\partial}{\partial x}x^n\,\psi = nx^{n-1}\frac{h}{2\pi i}\psi + x^n\frac{h}{2\pi i}\frac{\partial\psi}{\partial x}$$

hence $[x^n, p_x] = nx^{n-1}\dfrac{h}{2\pi i}$

5. (a) Let $\hat{A}$ and $\hat{B}$ be two hermitian operators that commute. Then the integral

$$\int\psi^*(\hat{A}\hat{B})\psi d\tau = \int \psi^*\hat{B}\hat{A}\psi\, d\tau = \int (\hat{A}\psi)\hat{B}^*\psi^*\, d\tau$$

$$= \int (\hat{B}\psi)^*(\hat{A}\psi)\, d\tau = \int \psi\cdot\hat{A}^*\cdot(\hat{B}\psi)^*\, d\tau = \int \psi\cdot(\hat{A}\hat{B})^*\psi^*\, d\tau$$

(b) $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{I}$

Since the unit operator $\hat{I}$ is hermitian, it follows from (a) that $\hat{A}^{-1}$ is hermitian.

6. $\psi = A\exp\left(\dfrac{2\pi i}{h}\lambda\phi\right)$, where A is the normalisation factor. The normalisation integral must be unity, i.e.

$$\int_0^{2\pi} \psi^*\psi\, d\phi = 1$$

or
$$A^2\int_0^{2\pi}\exp\left(-\frac{2\pi i}{h}\lambda\phi\right)\cdot\exp\left(\frac{2\pi i}{h}\lambda\cdot\phi\right)d\phi = 1$$

or
$$A^2\int_0^{2\pi} d\phi = 1$$

or
$$A = \frac{1}{\sqrt{2\pi}}$$

The normalised eigenfuncion is

$$\frac{1}{\sqrt{2\pi}}\exp\left(\frac{2\pi i}{h}\lambda\,\phi\right)$$

7. See Eqs. (2.49) for definition of $\hat{L}_z$ and $\hat{L}^2$ in polar coordinates. Since θ and ϕ are independent of each other and $\partial/\partial\phi$ commutes with $\partial^2/\partial\phi^2$ one proves that $\hat{L}_z$ commutes with $\hat{L}^2$.

8. If this function is integrated with respect to x between ± ∞ we obtain

$$\int_{-\infty}^{+\infty}\left(\frac{n}{\pi}\right)^{1/2}\exp(-nx^2)\,dx$$

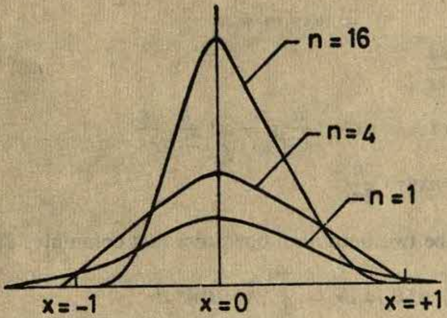
$$=\left(\frac{n}{\pi}\right)^{1/2}\int_{-\infty}^{+\infty}\exp(-nx^2)dx$$

$$=\left(\frac{n}{\pi}\right)^{1/2}\left(\frac{\pi}{n}\right)^{1/2}=1$$

A standard integral is given as,

$$\int_{-\infty}^{+\infty}\exp(-a^2x^2)\,dx=\frac{\sqrt{\pi}}{a}$$

The function also shows that as n increases at $x = 0$, the value of the function increases as shown in the following figure.

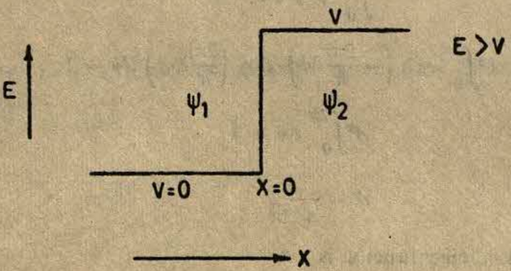


When n becomes infinite the function is zero everywhere except at $x = 0$ where it is infinite in such a way that the area under the curve is unity.

9. (a) Yes (b) $-2x + 1$.
10. 0, 1

Chapter 3

1. Consider the following potential barrier,



Then the wave equations for the two regions are

$$\frac{\partial^2\psi_1}{\partial x^2}+k_1^2\psi_1=0 \text{ where } k_1^2=\frac{8\pi^2 mE}{h^2}$$

$$\frac{\partial^2\psi_2}{\partial x^2}+k_2^2\psi_2=0 \text{ where } k_2^2=\frac{8\pi^2 m}{h^2}(E-V)$$

Their solutions are

$$\psi_1 = A\exp(ik_1x)+B\exp(-ik_1x)$$

$$\psi_2 = C\exp(ik_2x)+D\exp(-ik_2x)$$

Since there is nothing to cause reflection in the region 2, $D = 0$, we have

$$\psi_2 = C \exp(ik_2 x)$$

Since ψ and $\partial\psi/\partial x$ are single valued and continuous we have, at $x = 0$

$$\psi_1 = \psi_2$$

$$\frac{\partial\psi_1}{\partial x} = \frac{\partial\psi_2}{\partial x}$$

These give rise to the following equations

$$A + B = C$$

$$A - B = Ck_2/k_1$$

The reflection coefficient is defined by $\left|\frac{B}{A}\right|^2$ where

$$\left|\frac{B}{A}\right| = \left|\frac{k_1 - k_2}{k_1 + k_2}\right| < 1$$

2. For a box of length l

$$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi}{l} \cdot x \text{ where } n = 1, 2, 3, \ldots$$

$$\bar{p}x = \int_0^l \psi^* \left(\frac{h}{2\pi i} \frac{\partial}{\partial x}\right) \psi \, dx$$

$$= \frac{h}{2\pi i} \frac{2}{l} \int_0^l \sin \frac{n\pi x}{l} \cos \frac{n\pi x}{l} \cdot \frac{n\pi}{l} dx$$

$$= \frac{h}{\pi i} \frac{n\pi}{l^2} \int_0^l \sin \frac{2n\pi x}{l} dx = \frac{h}{\pi i} \frac{n\pi}{l^2} \times 0 = 0$$

$$\overline{p_x^2} = \int_0^l \psi^* \left(-\frac{h^2}{4\pi^2} \frac{\partial^2}{\partial x^2}\right) \psi \, dx$$

$$= \frac{h^2 n^2}{4l^2}$$

Hence the mean deviation $\overline{p_x^2} - (\overline{px})^2 \neq 0$. Therefore px is not definitely known.

3. The energy spectrum of a particle in a three dimensional box of unequal length (a, b, c) is given by

$$E(n_1 n_2 n_3) = \frac{h^2}{8m}\left[\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right]$$

For the lowest state $n_1 = n_2 = n_3 = 1$

Hence $$E_{111} = \frac{\overline{h^2}}{8m}\left[\frac{1}{a^2} + \frac{1}{b^2} \frac{1}{c^2}\right]$$

$$= \frac{6.6 \times 6.6 \times 10^{-54}}{8 \times 9.1 \times 10^{-28}}\left[\frac{1}{10^{-26}} + \frac{1}{2.25 \times 10^{-26}} + \frac{1}{4 \times 10^{-26}}\right]$$

$$= \frac{6.6 \times 6.6 \times 16.25}{8 \times 9.1 \times 9} = 1.014 \text{ erg}$$

4. For a box of length l, the classical probability for the square of the positional coordinate, x is given by

$$\overline{x^2} = \int_0^l x^2 \, dx \Big/ \int_0^l dx = l^3/3l = l^2/3$$

Quantum mechanically $\overline{x^2}$ is given by

$$\overline{x}^2 = \frac{\int_0^l \sin^2 \frac{n\pi x}{l} \cdot x^2\, dx}{\int_0^l \sin^2 \frac{n\pi}{l} \times dx}$$

$$= \frac{l^2}{3}\left(1 - \frac{3}{2n^2\pi^2}\right)$$

The result shows that for a very large value of n

$$\overline{x}^2 = l^2/3$$

which is the classical result. This is an example of *Bohr*'s *correspondence principle.*

5. The energy of an electron moving in a ring of zero potential field with a linear velocity v is given by

$$E = \tfrac{1}{2} m_e v^2$$

$$= \tfrac{1}{2} m_e \omega^2 r^2 = \tfrac{1}{2} I \omega^2 = \frac{L^2}{2I}$$

where ω is the angular velocity, and $L(= \omega I)$ the angular momentum. Therefore, the hamiltonian

$$\hat{H} = \frac{\hat{L}}{2I}$$

$$= -\frac{h^2}{8\pi^2 I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

[See Eq. (2.49)]

The wave equation is

$$\hat{H}\psi = E\psi.$$

Since we are dealing with an electron moving in a ring, ψ of such a system is independent of θ, $\theta = 90°$ for the ring. We have therefore

$$-\frac{h^2}{8\pi^2 I}\frac{\partial^2\psi}{\partial\phi^2} = E\psi$$

or

$$\frac{d^2\psi}{\partial\phi^2} + \frac{8\pi^2 I}{h^2}E\psi = 0$$

The well-behaved solutions of this equation must obey the condition

$$\psi(\phi) = \psi(2\pi + \phi)$$

As a result, we have for the acceptable solutions

$$\psi = \exp(im\phi)$$

where $m^2 = \frac{8\pi^2 I}{h^2}E$ and $m = 0, \pm 1, \pm 2, \pm 3 \ldots$. The energy spectrum is given by

$$E = \frac{m^2 h^2}{8\pi^2 I}$$

Each energy level except for $m = 0$, is doubly degenerate. It is possible to write the solution ψ as

$$\psi = A \sin m\phi + B \cos m\phi.$$

6. The energy spectrum according to Eq. (3.70) is given as

$$E = \frac{l(l+1)}{8\pi^2 I}h^2$$

where $$I = \mu r^2 = \frac{m_H m_{Br}}{m_H + m_{Br}} \cdot r^2$$

The first few energy levels are:

$$l = 0 \qquad E_0 = 0 \qquad m_H = 1$$

$$m_{Br} = 80$$

$$l = 1 \qquad E_1 = \frac{h^2}{4\pi^2 I} \qquad r = 1.42\hat{A}$$

$$l = 2 \qquad E_2 = \frac{3}{4}\frac{h^2}{\pi^2 I}$$

$$l = 3 \qquad E_3 = \frac{3}{2}\frac{h^2}{\pi^2 I}$$

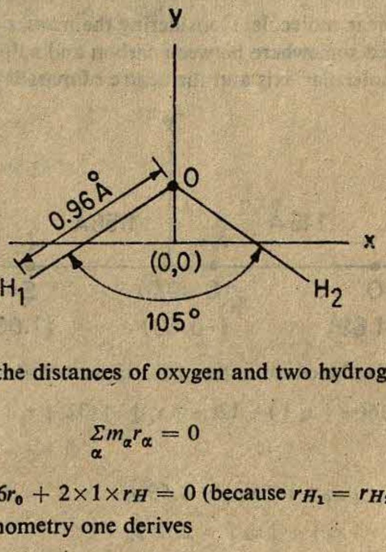
Since for each value of l, m can take values of $0, \pm 1, \pm 2 \ldots \pm l$, except for $l = 0$, all the levels are degenerate. Thus, the level with $l = 1$ is three-fold degenerate, the level with $l = 2$, five-fold degenerate, etc.

The lowest transition energy (i.e. for the transition $l = 0$ to $l = 1$) is given by

$$\Delta E = \frac{h^2}{4\pi^2 I}$$

The reader is asked to do the numerical calculations and to find out ΔE in Å.

7. We assume that the centre of mass is located at the origin of the coordinate system shown in the following figure for H_2O.



Let r_0, r_{H_1}, r_{H_2} be the distances of oxygen and two hydrogen from the centre of mass. Then

$$\sum_{\alpha} m_\alpha r_\alpha = 0$$

i.e., $$16 r_0 + 2 \times 1 \times r_H = 0 \text{ (because } r_{H_1} = r_{H_2} = r_H)$$

From simple trigonometry one derives

$$\begin{aligned} r_H^2 &= [0.96 \cos 52.5^\circ - r_0]^2 + [0.96 \sin 52.5^\circ]^2 \\ &= [0.58 - r_0]^2 + [0.76]^2 \\ &= [0.58 - r_0]^2 + 0.58 \end{aligned}$$

$$16 r_0 + 2 \cdot \sqrt{0.58 + (0.58 - r_0)^2} = 0$$

i.e., $$r_0 = 0.11 \qquad r_H = 0.89$$

The (x, y) coordinates of the atoms are as follows

$$O(0.0, -0.11) \qquad H_1(-0.76, -0.47) \qquad H_2(0.76, -0.47)$$

We now compute the moment of inertia tensor of water about its centre of mass. Since the molecule is in the x-y plane, the z-coordinates of all atoms are zero. We have

$$
\begin{aligned}
I_{xx} &= \sum_{\alpha} m_\alpha(r_\alpha^2 - x_\alpha^2) = \sum_{\alpha} m_\alpha(y_\alpha + z_\alpha^2) \\
&= 16\times(0.11)^2 + 1\times(0.47)^2 + 1\times(0.47)^2 \\
&= 0.63
\end{aligned}
$$

Since $m_H = 1.67\times10^{-24}$ g $\quad (1\,\text{Å})^2 = 10^{-16}$ cm^2

$$I_{xx} = 1.05\times10^{-40} \text{ g cm}^2$$

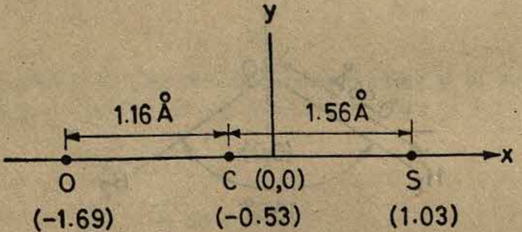
By a similar procedure

$$
\begin{aligned}
I_{yy} &= 1.94\times10^{-40} \text{ g cm}^2 \\
I_{zz} &= 3.00\times10^{-40} \text{ g cm}^2 \\
I_{xy} &= -\Sigma m_\alpha x_\alpha y_\alpha = -[16\times1\times0.11 + 1\times0.76\times-0.47 \\
&\quad +1\times0.76\times0.47] = 0
\end{aligned}
$$

In a similar function one obtains the following diagonal matrix

$$
I = \begin{pmatrix} 1.05\times10^{-40} & 0 & 0 \\ 0 & 1.94\times10^{-40} & 0 \\ 0 & 0 & 3.00\times10^{-40} \end{pmatrix}
$$

The O-C-S is a linear molecule. Considering the masses of the atoms the centre of mass will be located somewhere between carbon and sulphur. Let us assume that the x-axis is the molecular axis and the centre of mass is at the origin.



Let x_0, x_c and x_s be the coordinates of the indicated atoms. We then have

$$16(-|x_0|) + 12(-|x_c|) + 32.\,|x_s| = 0$$

From the figure

$$
\begin{aligned}
|x_c| + |x_s| &= 1.56 \text{ Å} \\
|x_0| + |x_s| &= 2.72 \text{ Å} \\
-16.\,(2.72 - |x_s|) - 12(1.56 - |x_s|) + 32\,|x_s| &= 0 \\
|x_s| &= 1.03 \\
|x_0| &= 1.69 \\
|x_c| &= 0.53
\end{aligned}
$$

The x-coordinates of the atoms are shown in the figure. We now compute the moment of intertia tensor

$$I_{xx} = \sum_{\alpha} m_\alpha(y_\alpha^2 + z_\alpha^2) = 0$$

$$I_{yy} = \sum_{\alpha} m_\alpha (x^2 + z^2)$$

$$= 16\times(1.69)^2 + 12\times(0.53)^2 + 32(1.03)^2$$

$$= 83$$

In gm·cm² units

$$I_{yy} = 83\times 1.67\times 10^{-40} \doteq 1.38\times 10^{-38} \text{ g cm}^2$$

$$I_{zz} = 1.38\times 10^{-38} \text{ g cm}^2$$

$$I_{xy} = I_{yx} = I_{zx} = 0$$

We have then the following matrix

$$I = \begin{pmatrix} 1.38\times 10^{-38} & 0 & 0 \\ 0 & 1.38\times 10^{-38} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

8. $\dfrac{B}{hc} = \dfrac{h^2}{8\pi^2 Ihc} = 10.6 \text{ cm}^{-1}$ [see Eq. (3.109)]

$$h = 6.624\times 10^{-34} \text{ J s}$$

$$\hbar = \frac{h}{2\pi} = 1.054\times 10^{-34} \text{ J s}$$

$$c = 2.998\times 10^{10} \text{ cm/s}$$

$$I = \frac{\hbar}{4\pi c\times 10.6} = \frac{1.054\times 10^{-34}}{4\times 3.14\times 2.998\times 10^{10}\times 10.6} \text{ J s}^2$$

$$= 0.3\times 10^{-46} \text{ J s}^2$$

The angular velocity ω is given by

$$L^2 = I^2\omega^2$$

Since eigenvalues of $\hat{L}^2$ is $l(l+1)\hbar^2$

we have $$\omega = \frac{l(l+1)\hbar}{I}$$

Period of rotation $\tau_{\text{rot}} = \dfrac{2\pi}{\omega} = \dfrac{2\pi I}{\sqrt{l(l+1)}\hbar}$

$$\tau_{\text{rot}} = \frac{2\times 3.14\times 0.3\times 10^{-46} \text{ J s}^2}{\sqrt{4\times 5}\times 1.054\times 10^{-34} \text{ J s}}$$

$$= 2.7\times 10^{-12} \text{ s}$$

9. (a) 1 (b) 6 (c) 4

10.

E_J(KJ/M)	0	2.9	8.7	17.5	29.1
Orientations	1	3	5	7	9

Chapter 4

1. The zero-point energy of a harmonic oscillator is given by

$$E_0 = \tfrac{1}{2}h\nu_0 = \tfrac{1}{2}h\,\frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$= \frac{h}{4\pi}\sqrt{\frac{k}{m}}$$

where

$$k = 10^4 \text{ dyne/cm}$$
$$m = 1.67\times10^{-24} \text{ gm}$$

Hence

$$E_0 = 10^{-13} \text{ erg.}$$

2. The mean value of the potential energy of an electron in the $1s$-orbital of a H-atom is given by

$$-\overline{\frac{1}{r}} = -\int_0^\infty \int_0^\pi \int_0^{2\pi} 1s\cdot\frac{1}{r}\cdot 1s\, r^2\, dr \sin\theta\, d\theta\, d\phi$$

where $$1s = \frac{1}{\sqrt{\pi}}\exp(-r)$$

Hence

$$-\overline{\frac{1}{r}} = -\frac{1}{\pi}\int_0^\infty \exp(-2r)\, r\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi$$
$$= -1.0 \text{ (a.u.)}$$

The total energy of an electron in $1s$-orbital is -0.5 a.u. [Eq. (4.110)]. Thus, the mean kinetic energy is $+0.5$ a.u. and the theorem is proved. This theorem is known as the *Virial theorem.*

3. The normalisation integral for ϕ_1 is

$$\int \phi_1^*\phi_1\, d\tau = 1$$

i.e. $$N_1^2 \int_0^\infty \exp(-2r)\, r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 1$$

i,e. $$4\pi N_1^2 \int_0^\infty \exp(-2r) r^2\, dr = 1$$

i.e. $$4\pi N_1^2 \int \frac{2}{(2)^3} = 1$$

$$N_1^2 = 1/\pi \quad \text{or} \quad N_1 = 1/\sqrt{\pi}$$

Similarly

$$\int \phi_2^*\phi_2\, d\tau = 1$$

i.e. $$4\pi N_2^2 \int_0^\infty \exp(-2r)\, r^4\, dr = 1$$

i.e. $$4\pi N_2^2 \frac{4!}{(2)^5} = 1, \text{ or } N_2 = \frac{1}{\sqrt{3\pi}}$$

According to the Schmidt orthogonalisation procedure (described in Sec. 2.6) the pair of orthogonal functions is given by

$$\psi_1 = \phi_1$$
$$\psi_2 = \phi_1 - \frac{1}{\int \phi_1\phi_2\, d\tau}\phi_2$$

where

$$\int \phi_1\phi_2 \, d\tau = N_1N_2 4\pi\int_0^\infty \exp(-2r)r^3 \, dr = N_1N_2\cdot 4\pi\cdot\frac{3!}{(2)^4}$$

$$= \frac{\sqrt{3}}{2}$$

4. This is a statement of the *Unsold theorem*.

We shall show that $|Y_{1,0}|^2 + |Y_{1,1}|^2 + |Y_{1,1}|^2$ and $|Y_{2,0}|^2 + |Y_{2,1}|^2 + |Y_{2,-1}|^2 + |Y_{2,2}|^2 + |Y_{2,-2}|^2$ where Y's are the spherical harmonics are independent of θ and ϕ.

$$|Y_{1,0}|^2 + |Y_{1,1}|^2 + |Y_{1,-1}|^2$$

$$= \left(\frac{\sqrt{3}}{2\sqrt{\pi}}\right)^2 \cos^2\theta + \left(\frac{\sqrt{3}}{2\sqrt{2\pi}}\right)^2 \sin^2\theta + \left(\frac{\sqrt{3}}{2\sqrt{2\pi}}\right)^2 \sin^2\theta$$

$$= \left(\frac{\sqrt{3}}{2\sqrt{\pi}}\right)^2 (\cos^2\theta + \sin^2\theta) = \frac{3}{4\pi}$$

$$|Y_{2,0}|^2 + |Y_{2,1}|^2 + |Y_{2,-1}|^2 + |Y_{2,2}|^2 + |Y_{2,-2}|^2$$

$$= \left(\frac{\sqrt{5}}{4\sqrt{\pi}}\right)^2 (3\cos^2\theta - 1)^2 + 2\left(\frac{\sqrt{15}}{4\sqrt{1\pi}}\right)^2 \sin^2 2\theta + 2\left(\frac{\sqrt{15}}{4\sqrt{2\pi}}\right)^3 \sin^4\theta$$

$$= \left(\frac{\sqrt{5}}{4\sqrt{\pi}}\right)^2 [(3\cos^2\theta - 1)^2 + 3\sin^2\theta\,(3\cos^2\theta + 1)]$$

$$= \left(\frac{\sqrt{5}}{4\sqrt{\pi}}\right)^2 \cdot 4 = \frac{5}{4\pi}$$

5. We write Eq. (4.120) in wave number ω [$E = hc\omega$] as

$$\omega = (n + 1/2)\omega_0 - (n + 1/2)^2 x_0\omega_0$$

So, for the 0 → 1 transition

$$\omega_1 = 3917.44 - 1331.80 = 2585.6 \text{ cm}^{-1}$$

$$= 3/2\omega_0 - (3/2)^2 x_0\omega_0 - 1/2\omega_0 + (1/2)^2 x_0\omega_0$$

$$= \omega_0 - 2x_0\omega_0$$

For the 0 → 2 transition

$$\omega_2 = 6398.94 - 1331.84 = 5067.1 \text{ cm}^{-1}$$

$$= 2\omega_0 - 6x_0\omega_0$$

Thus, from the two equations

$$2586 = \omega_0(1 - 2x_0)$$

$$5067 = 2\omega_0(1 - 3x_0)$$

We get

$$\omega_0 = 2693 \text{ cm}^{-1}$$

$$x_0 = 0.0198$$

At the dissociation limit E_{vib} is maximum. Differentiating Eq. (4.120) with respect to n and setting the corresponding derivative equal to zero.

We have

$$\frac{dE_{\text{vib}}}{dn} = h\nu_0 - 2(n + 1/2)x_0 h\nu_0 = 0$$

$$(n + 1/2) = \frac{1}{2x_0}$$

Substituting this back into Eq. (4.120) and setting the corresponding E_{vib} equal to D_e we obtain

$$D_e = \frac{h\nu_0}{2x_0} - \frac{h\nu_0}{4x_0} = \frac{h\nu_0}{4x_0}$$

$$= \frac{hc_0\omega_0}{4x_0} = \frac{6.624\times10^{-27}\times2.99\times10^{10}\times2693}{4\times0.0198}\ \text{erg}$$

$$= 4.2\ \text{eV}\ [1\ \text{erg} = 6.24\times10^{11}\ \text{eV}]$$

7. HF (0.967 N cm^{-1}), HCl (0.516 N cm^{-1}), HBr (0.412 N cm^{-1}), HI (0.314 N cm^{-1}).

Chapter 5

1. We have to find out, at first, the normalisation factor, N in the trial wave function. The normalisation condition gives

$$N^2\int_0^1 x^{2a}(1-x^2)^2\,dx = 1$$

i.e.

$$N^2\left[\int_0^1 x^{2a}\,dx + \int_0^1 x^{2a+4}\,dx - 2\int_0^1 x^{2a+2}\,dx\right] = 1$$

or

$$N^2\left[\frac{1}{2a+1} + \frac{1}{2a+5} - \frac{2}{2a+3}\right] = 1$$

or

$$N^2 = \frac{(2a+1)(2a+5)(2a+3)}{8}$$

The energy is given by

$$E = -\frac{h^2}{8\pi^2 m_e}\int_0^1 N^2x^a(1-x^2)\frac{d^2}{dx^2}x^a(1-x^2)\,dx$$

$$= -\frac{h^2}{8\pi^2 m_e}N^2\frac{8a(a-1) - 8a(2a-1) - 4(2a-1)}{(2a+3)(2a+1)(2a-1)}$$

$$= -\frac{h^2}{8\pi^2 m_e}\frac{(2a+1)(2a+5)(2a+3)}{8}\cdot\frac{(-8a^2-8a+4)}{(2a+3)(2a+1)(2a-1)}$$

$$= -\frac{h^2}{8\pi^2 m_e}\left[\frac{-4a^3-14a^2-8a+5}{4a-2}\right]$$

$$= -\frac{1}{2}\left[\frac{-4a^3-14a^2-8a+5}{4a-2}\right]\ \text{(a.u.)} \qquad (1)$$

Setting

$$\frac{\partial E}{\partial a} = 0,\ \text{we get}$$

$$8a^3 + 8a^2 - 14a + 1 = 0$$

or

$$a = 0.862$$

Substituting this value of a in Eq. (1), we get the lowest energy

$$E = \frac{1}{2}\left[\frac{-4(0.862)^3 - 14(0.862)^2 - 8(0.862) + 5}{4(0.862) - 2}\right]\ \text{(a.u.)}$$

$$= +5.13\ \text{a.u.}$$

2. The energy is given by

$$E = \frac{\int_0^\infty \exp(-\alpha x^2)\left[-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial x^2} + 2\pi^2\nu^2x^2\right]\exp(-\alpha x^2)\,dx}{\int_{-\infty}^{\infty}\exp(-2\alpha x^2)\,dx} \tag{2}$$

The integral in the denominator of Eq. (2) may be written as

$$\int_{-\infty}^{\infty}\exp(-2\alpha x^2)\,dx = 2\cdot\int_0^\infty \exp(-2\alpha x^2)\,dx$$

$$= 2\cdot\frac{1}{2}\sqrt{\frac{\pi}{2\alpha}} = \sqrt{\frac{\pi}{2\alpha}}$$

where use is made of the following standard integral:

$$\int_0^\infty x^{2n}\exp(-ax^2)\,dx = \frac{1\cdot3\cdot5\cdot\ldots(2n-1)}{2^{n+1}}\sqrt{\frac{\pi}{a^{2n+1}}}$$

The numerator in Eq. (2) may be simplified as follows:

$$\exp(-\alpha x^2)\left[-\frac{h^2}{8\pi^2}\left(4\alpha^2 - \frac{16\pi^2\nu^2}{h^2}\right)x^2 - 2\alpha\right]\exp(-\alpha x^2)\,dx$$

$$= -\int_0^\infty \frac{h^2}{4\pi^2}\left\{\left(4\alpha^2 - \frac{16\pi^4\nu^2}{h^2}\right)x^2 - 2\alpha\right\}\exp(-2\alpha x^2)\,dx$$

$$= -\frac{h^2}{4\pi^2}\left(4\alpha^2 - \frac{16\pi^4\nu^2}{h^2}\right)\int_0^\infty \exp(-2\alpha x^2)x^2\,dx + \frac{h^2\alpha}{2\pi^2}\int_0^\infty \exp(-2\alpha x^2)\,dx$$

$$= -\frac{h^2}{4\pi^2}\left(4\alpha^2 - \frac{16\pi^4\nu^2}{h^2}\right)\cdot\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}} + \frac{h^2\alpha}{2\pi^2}\cdot\frac{1}{2}\cdot\sqrt{\frac{\pi}{2\alpha}}$$

$$= \left[-\frac{h^2\alpha^2}{\pi^2 8\alpha} + \frac{4\pi^2\nu^2}{8\alpha} + \frac{h^2\alpha}{4\pi^2}\right]\sqrt{\frac{\pi}{2\alpha}}$$

$$= \left[\frac{\pi^2\nu^2}{2\alpha} + \frac{h^2\alpha}{8\pi^2}\right]\sqrt{\frac{\pi}{2\alpha}} \tag{3}$$

Then Eqs. (1) and (3) give

$$E = \frac{\pi^2\nu^2}{2\alpha} + \frac{h^2\alpha}{8\pi^2} \tag{4}$$

The equation $\frac{\partial E}{\partial \alpha} = 0$ gives $\alpha = \frac{2\pi^2\nu}{h}$.

When this value of α is substituted in Eq. (4) we get the lowest energy, i.e.

$$E_0 = \tfrac{1}{2}h\nu$$

3. The perturbation hamiltonian:

$$\hat{H}^1 = e\epsilon\cdot x$$

$$= e\epsilon\frac{\xi}{\sqrt{\beta}}$$

where the variable x is changed to ξ. (See Sec. 4.1)

The first-order correction to the energy of the n^{th} quantum state of a harmonic oscillator is

$$\langle \psi_n | H' | \psi_n \rangle = \frac{e}{\sqrt{\beta}}\cdot\epsilon\cdot\langle \psi_n | \xi | \psi_n \rangle$$

$$= \frac{e\epsilon}{\sqrt{\beta}}\left[\frac{1}{2^n n!}\frac{1}{\sqrt{\pi}}\right]\int_{-\infty}^{\infty} \exp(-\xi^2)H_n(\xi)\xi H_n(\xi)\,d\xi$$

$$= 0 \text{ [according to Eq. (4.41)]}$$

The second-order correction to the energy is given by

$$\sum_{m \neq n} \frac{\langle \psi_m \mid H' \mid \psi_n \rangle^2}{E_n^0 - E_m^0}$$

Consider the integral, for $m \neq n$

$$\langle \psi_m \mid H' \mid \psi_n \rangle = \frac{e\epsilon}{\sqrt{\beta}} \langle \psi_m \mid \xi \mid \psi_n \rangle$$

$$= \frac{e\epsilon}{\sqrt{\beta}} \cdot \left[\frac{1}{2^m m!}\frac{1}{\sqrt{\pi}}\frac{1}{2^n n!}\frac{1}{\sqrt{\pi}}\right]^{\frac{1}{2}}\int_{-\infty}^{\infty} \exp(-\xi^2)H_m(\xi)\xi_1 H_n(\xi)\,d\xi$$

$$= 0, \text{ unless } m = n \pm 1 \text{ [see Eq. (4.41)]}$$

4. This is an application of Eq. (5.110), where r_{if}, in a.u. is given by

$$r_{if} = \langle 1s \mid r\cos\theta \mid 2p_0 \rangle = \left(\frac{2}{3}\right)^5 \frac{2^3}{\sqrt{2}}$$

where $1s$- and $2p_0$ are the wave functions of the $1s$ and $2p_0$-orbitals of the hydrogen atom. 1 a.u. of electric dipole = 2.4×10^{-18} e.s.u.

5. If a hydrogen atom is placed in a small uniform electric field $\mid \mathbf{E}_0 \mid$ acting in the z-direction, then the perturbation on the electron is

$$\hat{V} = e \mid \mathbf{E}_0 \mid z$$

$$= e \mid \mathbf{E}_0 \mid r\cos\theta$$

According to the first-order perturbation theory the $1s$-wave-function of the hydrogen atom is given by

$$1s = 1s^0 + e \mid \mathbf{E}_0 \mid \left[\frac{\langle 1s_0 \mid r\cos\theta \mid 2s^0 \rangle}{E_{1s^0} - E_{2s^0}}(2s^0) + \frac{\langle 1s^0 \mid r\cos\theta \mid 2p_z^0 \rangle}{E_{1s^0} - E_{2p_0}}(2p_z^0) + \frac{\langle 1s^0 \mid r\cos\theta \mid 3p_z^0 \rangle}{E_{1s}^0 - E_{3p}^0}(3p_z^0) + \ldots\right]$$

Similarly the $2s$-wavefunction in the perturbation field is given by

$$2s = 2s^0 + e \mid \mathbf{E}_0 \mid \left[\frac{\langle 2s^0 \mid r\cos\theta \mid 1s^0 \rangle}{E_{2s^0} - E_{1s^0}}(1s_0) + \frac{\langle 2s^0 \mid r\cos\theta \mid 2p_z^0 \rangle}{E_{2s^0} - E_{2p^0}}(2p^0) + \ldots\right]$$

The integral $\langle 1s^0 \mid r\cos\theta \mid 2s^0 \rangle = 0$ [see Eq. (5.35)].

The nonvanishing terms are $\langle 1s^0 \mid r\cos\theta \mid 2p_z^0 \rangle$. $\langle 2s^0 \mid r\cos\theta \mid 2p_z^0 \rangle$, $\langle 1s^0 \mid r\cos\theta \mid 3p_z^0 \rangle$, etc. One may write

$$1s = 1s^0 + \lambda 2p_z^0 + \lambda' 3p_z^0 + \ldots$$

$$2s = 2s^0 + \eta 2p_z^0 + \eta' 3p_z^0 + \ldots$$

where λ, λ', η and η' are non-zero constants proportional to $\mid \mathbf{E}_0 \mid$. We shall now consider the transition dipole integral between the perturbed $1s$ and $2s$ states of the hydrogen atom

$$\langle 1s \mid r\cos\theta \mid 2s \rangle = \langle 1s^0 \mid r\cos\theta \mid 2s^0 \rangle + \eta \cdot \langle 1s^0 \mid r\cos\theta \mid 2p_z^0 \rangle$$

$$+ \lambda \langle 2s^0 \mid r\cos\theta \mid 2p_z^0 \rangle + \ldots$$

Except the first term on the right hand side of the above equation, which is zero, the other terms are nonvanishing. One of them is shown in the Problem 4. Thus a transition from the $1s$-state to the $2s$-state is possible in the presence of an electric field.

6. To obtain the second-order correction we start with Eq. (5.8)

$$(H^{(0)} - E^{(0)})\psi^{(2)} = -\hat{V}\psi^{(1)} + E^{(2)}\psi^{(0)} + E^{(1)}\psi^{(1)}$$

Let us now specify an eigenvalue $E_i^{(0)}$ and its corresponding eigenfunction $\psi_i^{(0)}$ of the unperturbed equation

$$H^{(0)}\psi_i^{(0)} = E_i^{(0)}\,\psi_i^{(0)}$$

with $i = 1, 2, 3, 4, \ldots$

$E_i^{(0)}$ is nondegenerate. Equation (5.8) for the ith level is

$$(H^{(0)} - E_i^{(0)})\psi_i^{(2)} = -\hat{V}\psi_i^{(1)} + E_i^{(2)}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(1)} \tag{1}$$

We now expand $\psi_i^{(2)}$ in terms of the complete set of the orthonormal functions $\psi_j^{(0)}$

$$\psi_i^{(2)} = \sum_{j\neq i} b_{ij}\,\psi_j^{(0)} \tag{2}$$

Substituting Eq. (2) in Eq. (1) we obtain

$$(H^{(0)} - E_i^{(0)}) \sum_{j\neq i} b_{ij}\,\psi_j^{(0)} = -\hat{V}\psi_i^{(1)} + E_i^{(2)}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(1)}$$

Multiplying both sides by $\psi_k^{(0)*}$ and integrating

$$\sum_{j\neq i} b_{ij}\,\langle \psi_k^{(0)*} \mid H^{(0)} \mid \psi_j^{(0)}\rangle - \sum_{j\neq i} b_{ij}\,E_i^{(0)}\langle \psi_k^{(0)} \mid \psi_j^{(0)}\rangle$$

$$= -\langle \psi_k^{(0)} \mid \hat{V} \mid \psi_i^{(1)}\rangle + E_i^{(2)}\langle \psi_k^{(0)*} \mid \psi_i^{(0)}\rangle + E_i^{(1)}\langle \psi_i^{(1)} \mid \psi_k^{(0)}\rangle$$

Since $\psi_k^{(0)}$, $\psi_j^{(0)}$ are orthonormal, we have

$$b_{ik}(E_k^{(0)} - E_i^{(0)}) = -\langle \psi_k^{(0)} \mid \hat{V} \mid \psi_i^{(1)}\rangle + E^{(1)}\langle \psi_i^{(1)} \mid \psi_k^{(0)}\rangle \tag{3}$$

Since $$\psi_i^{(1)} = \sum_{j\neq i} \frac{\langle \psi_j^{(0)} \mid \hat{V} \mid \psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}\,\psi_j^{(0)} \qquad \text{[see Eq. (5.27)]}$$

$$E_i^{(1)} = \langle \psi_i^{(0)} \mid \hat{V} \mid \psi_i^{(0)}\rangle \qquad \text{[see Eq. (5.24)]}$$

we write Eq. (3) as

$$b_{ik}(E_k^{(0)} - E_i^{(0)}) = -\sum_{j\neq i} \frac{\langle \psi_k^{(0)} \mid \hat{V} \mid \psi_j^{(0)}\rangle\langle \psi_j^{(0)} \mid \hat{V} \mid \psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}$$

$$+ \sum_{j\neq i} \langle \psi_i^{(0)} \mid \hat{V} \mid \psi_i^{(0)}\rangle\langle \psi_k^{(0)} \mid \psi_j^{(0)}\rangle \frac{\langle \psi_j^{(0)} \mid \hat{V} \mid \psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}$$

$$b_{ik} = -\sum_{j\neq i} \frac{\langle \psi_i^{(0)} \mid \hat{V} \mid \psi_j^{(0)}\rangle\langle \psi_j^{(0)} \mid \hat{V} \mid \psi_k^{(0)}\rangle}{(E_i^0 - E_j^0)(E_k^0 - E_i^0)}$$

$$- \frac{\langle \psi_i^{(0)} | \hat{V} | \psi_i^{(0)} \rangle \langle \psi_k^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_i^0 - E_k^0)^2} \tag{4}$$

Therefore one may write

$$\psi_i^{(2)} = \sum_{k \neq i} b_{ik} \psi_k^{(0)}$$

$$= \sum_{\substack{k \neq i \\ j \neq i}} \left\{ \frac{\langle \psi_i^{(0)} | \hat{V} | \psi_i^{(0)} \rangle \langle \psi_j^{(0)} | \hat{V} | \psi_k^{(0)} \rangle}{(E_i^{(0)} - E_j^{(0)})(E_i^{(0)} - E_k^{(0)})} - \frac{\langle \psi_i^{(0)} | \hat{V} | \psi_i^{(0)} \rangle \langle \psi_k^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_i^0 - E_k^0)^2} \right\} \psi_k^{(0)}$$

7. $C = 8/9\pi$, $E = -0.424$ (a.u.)

Chapter 6

We may write the unperturbed hamiltonian as

$$H^{(0)} = H_1^{(0)} + H_2^{(0)}$$

where
$$H_i^{(0)} = -\tfrac{1}{2}\nabla_i^2 - \frac{2}{r_i} \quad (i = 1, 2)$$

and
$$H_i^0 \psi_{(i)}^{(0)} = E_{(i)}^{(0)} \psi_{(i)}^{(0)}$$

with $E_{(i)}^{(0)} = -2, 0$ (a.u.) [see Eqs. (4.113) and (4.114)]
We may suppose that the eigenfunction of the unperturbed hamiltonian $H^{(0)}$ can be written as the simple product

$$\psi_{(1,2)}^{(0)} = \psi_{(1)}^{(0)} \psi_{(2)}^{(0)}$$

where $\psi_{(i)}^{(0)}$ is the wavefunction of the ith electron for a hydrogen-like-atom with $Z = 2$. We may write then

$$\begin{aligned} H^{(0)} \psi_{(1,2)}^{(0)} &= H_1^{(0)} \psi_{(1)}^{(0)} \cdot \psi_{(2)}^{(0)} + H_{(2)}^{(0)} \psi_{(1)}^{(0)} \psi_{(2)}^{(0)} \\ &= -(2 + 2) \psi_{(1)}^{(0)} \psi_{(2)}^{(0)} \\ &= -4.0 \psi_{(1,2)}^{(0)} \end{aligned} \tag{1}$$

The first-order perturbation energy using the electron repulsion as the perturbation is given by

$$\begin{aligned} E^{(1)} &= \left\langle \psi_{(1,2)}^{(0)} \left| \frac{1}{r_{12}} \right| \psi_{(1,2)}^{(0)} \right\rangle \\ &= \left\langle \psi_{(1)}^{(0)} \psi_{(2)}^{(0)} \left| \frac{1}{r_{12}} \right| \psi_{(1)}^{(0)} \psi_{(2)}^{(0)} \right\rangle \end{aligned} \tag{2}$$

For the ground state of helium

$$\psi_{(1)}^{(0)} = \psi_{(2)}^{(0)} = \left[\frac{2^3}{\pi} \right]^{1/2} \exp(-2r_1) \text{ [or } \exp(-2r_2)]$$

The integral in Eq. (2) can therefore, be written as

$$E^{(1)} = \frac{2^6}{\pi^2}\iint \frac{\exp(-4r_1)\exp(-4r_2)}{r_{12}}\, d\tau_1\, d\tau_2 \tag{3}$$

where $d\tau_1 = r_1^2\, dr_1 \sin\theta\, d\theta_1\, d\phi_1$

$$d\tau_2 = r_2^2\, dr_2 \sin\theta_2\, d\theta_2\, d\phi_2$$

An integral similar to that of Eq. (3) is worked out in Appendix 6. Thus we have

$$E^{(1)} = \frac{5}{4} \tag{4}$$

Therefore, the ground state energy of helium follows from Eqs. (1) and (4)

$$E = E^{(0)} + E^{(1)}$$

$$= -4{\cdot}0 + \frac{5}{4} = -2{\cdot}75 \text{ a.u.}$$

$$= -74{\cdot}80 \text{ eV}$$

2. $\langle \psi_i \mid L_+ \mid \psi_j \rangle = \langle \psi_i \mid L_x + iL_y \mid \psi_j \rangle = \langle \psi_i \mid L_x \mid \psi_j \rangle + i\langle \psi_i \mid L_y \mid \psi_j \rangle$

Since $\hat{L}_x$ and $\hat{L}_y$ are hermitian, according to turn-over rule we have

$$\langle \psi_i \mid L_+ \mid \psi_j \rangle = \langle \psi_j \mid L_x \mid \psi_i \rangle^* + i\langle \psi_j \mid L_y \mid \psi_i \rangle^* \tag{1}$$

Now

$$\langle \psi_j \mid L_+ \mid \psi_i \rangle^* = \langle \psi_j \mid L_x \mid \psi_i \rangle^* - i\langle \psi_j \mid L_y \mid \psi_i \rangle^* \tag{2}$$

So from Eqs. (1) and (2)

$$\langle \psi_i \mid L_+ \mid \psi_j \rangle \neq \langle \psi_j \mid L_+ \mid \psi_i \rangle$$

Similarly, $\hat{L}_-$ is also not hermitian.

But

$$\hat{L}_+\hat{L}_- = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z$$

$$\hat{L}_-\hat{L}_+ = \hat{L}_x^2 + \hat{L}_y^2 - \hat{L}_z$$

Since $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ are hermitian, the product operators $\hat{L}_-L_+$ and $\hat{L}_+\hat{L}_-$ are hermitian.

3. From Eqs. (6.82a) and (6.82b), we may write

$$\hat{L}_+\psi(2,0) = \sqrt{6}\,\psi(2,1)$$

$$\hat{L}_-\psi(2,0) = \sqrt{6}\,\psi(2,-1)$$

$$\hat{L}_+\psi(2,-1) = 2\psi(2,2)$$

$$\hat{L}_-\psi(2,-1) = 2\psi(2,-2)$$

But

$$\hat{L}_+\psi(2,2) = 0$$

$$\hat{L}_-\psi(2,-2) = 0$$

Since we are dealing with a two-electron problem, we have

$$\hat{L}_+ = \hat{l}_+(1) + \hat{l}_+(2)$$

$$\hat{L}_- = \hat{l}_-(1) + \hat{l}_-(2)$$

Therefore,

$$\hat{L}_+\psi_{(2,0)} = [\hat{l}_+(1) + \hat{l}_+(2)]\psi_{(2,0)}$$

$$= [\hat{l}_+(1) + \hat{l}_+(2)]\frac{1}{\sqrt{6}}\{2\,|\phi_0\bar{\phi}_0| + |\phi_{-1}\bar{\phi}_1| + |\phi_1\bar{\phi}_{-1}|\}$$

Operating on term by term, we obtain

$$[\hat{l}_+(1) + \hat{l}_+(2)]\,|\phi_0\bar{\phi}_0| = \sqrt{2}\,(|\phi_1\bar{\phi}_0| + |\phi_0\bar{\phi}_1|)$$

$$[\hat{l}_+(1) + \hat{l}_+(2)]\,|\phi_{-1}\bar{\phi}_1| = \sqrt{2}\cdot|\phi_0\bar{\phi}_1|$$

$$(\text{because } \hat{l}_+(2)\bar{\phi}_1(2) = 0)$$

$$[\hat{l}_+(1) + \hat{l}_+(2)]\,|\phi_1\bar{\phi}_{-1}| = \sqrt{2}\,|\phi_1\bar{\phi}_0|$$

$$[\text{because } \hat{l}_+(1)\phi_1(1) = 0].$$

Hence

$$\hat{L}_+\psi_{(2,0)} = \sqrt{\frac{2}{6}}\{3[|\phi_1\bar{\phi}_0| + |\phi_0\bar{\phi}_1|]\}$$

$$= \sqrt{3}\,[|\phi_1\bar{\phi}_0| + |\phi_0\bar{\phi}_1|]$$

But we have seen that

$$\hat{L}_+\psi_{(2,0)} = \sqrt{6}\,\psi_{(2,1)}$$

Hence

$$\psi_{(2,1)} = \frac{1}{\sqrt{2}}\,[\,|\phi_1\bar{\phi}_0| + |\phi_0\bar{\phi}_1|\,]$$

We now operate on $\psi_{(2,0)}$ with $\hat{L}_-$, term by term

$$[\hat{l}_+(1) + \hat{l}_+(2)]\,|\phi_0\bar{\phi}_0| = \sqrt{2}\,(\,|\phi_0\bar{\phi}_0| + |\phi_0\bar{\phi}_{-1}|\,)$$

$$[\hat{l}_-(1) + \hat{l}_-(2)]\,|\phi_{-1}\bar{\phi}_1| = \sqrt{2}\,|\phi_{-1}\bar{\phi}_0|$$

$$(\text{because } l_+(1)\phi_{-1}(1) = 0)$$

$$[\hat{l}_-(1) + l_-(2)]\,|\phi_1\bar{\phi}_{-1}| = \sqrt{2}\cdot|\phi_0\bar{\phi}_{-1}|$$

$$(\text{because } \hat{l}_-(2)\phi_{-1}(2) = 0)$$

Thus

$$\hat{L}_-\psi_{(2,0)} = \sqrt{\frac{2}{6}}\{3[\,|\phi_{-1}\bar{\phi}_0| + |\phi_0\bar{\phi}_{-1}|\,]\}$$

$$= \sqrt{3}\,[\,|\phi_{-1}\bar{\phi}_0| + |\phi_0\bar{\phi}_{-1}|\,]$$

But we have seen that

$$L_-\psi_{(2,0)} = \sqrt{6}\,\psi_{(2,-1)}$$

Hence

$$\psi_{(2,-1)} = \frac{1}{\sqrt{2}}\{\,|\phi_{-1}\bar{\phi}_0| + |\phi_0\bar{\phi}_{-1}|\,\}$$

Carrying on like this we obtain

$$\psi_{(2,2)} = |\, \phi_1 \bar{\phi}_1 \,|$$
$$\psi_{(2,-2)} = |\, \bar{\phi}_{-1} \phi_{-1} \,|$$

It is to be noted that the normalisation factor in front of each determinant is omitted in this problem.

4. For an electron in a *d*-orbital ($l = 2$) there are two values of j, $j = 3/2, 5/2$.

The operator $\hat{J}^2$ is given as

$$\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}.\hat{S}$$

or

$$\hat{L}.\hat{S} = \tfrac{1}{2}[\hat{J}^2 - \hat{L}^2 - \hat{S}^2]$$

The first-order perturbation energy is given by

$$E' = \langle d \,|\, \xi \hat{L}.\hat{S} \,|\, d \rangle$$

$$= \tfrac{1}{2}\xi[\langle d \,|\, \hat{J}^2 \,|\, d \rangle - \langle d \,|\, L^2 \,|\, d \rangle - \langle d \,|\, S^2 \,|\, d \rangle]$$

where *d* is written for the wave function of a *d*-orbital.
Since

$$\langle d \,|\, \hat{J}^2 \,|\, d \rangle = j(j+1)$$

$$\langle d \,|\langle \hat{L}^2 \,|\, d \rangle = l(l+1) = 2\cdot 3 = 6$$

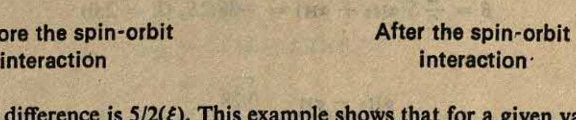
$$\langle d \,|\, \hat{S}^2 \,|\, d \rangle = S(S+1) = \tfrac{1}{2}\cdot\tfrac{3}{2} = \tfrac{3}{4}$$

We have

$$E' = \tfrac{1}{2}\xi[j(j+1) - 6 - 3/4]$$

There are two values of j, so that

$$E'(^2D_{5/2}) = \xi$$
$$E'(^2D_{3/2}) = -3/2(\xi)$$


$^2D_{5/2}$
$^2D_{3/2}$
$^2D_{5/2}$
$5/2\,\xi$
$^2D_{3/2}$
Before the spin-orbit interaction
After the spin-orbit interaction

The energy difference is $5/2(\xi)$. This example shows that for a given value of l, the state having smaller j is more stable.

5. For a closed shell configuration it can be easily proved that

$$M_s = M_L = 0$$

Therefore, the electronic state is represented by ^1S.

6. $^4S_{3/2}$

Chapter 7

1. C_2+ and B_2+ have the following electron configurations (see Table 7.1)

$$C_2+\cdot[Li_2](\sigma_u 2s)^2(\pi_u 2p)^3$$
$$B_2+\cdot[Li_2](\sigma_u 2s)^2(\pi_u 2p)^1$$

There are three electrons in the $\pi_u 2p$ shell of C_2+ and one electron in the $(\pi_u 2p)$ shell of B_2+. They give rise to same states, namely, $^2\pi_u$.

2. Let us assume that the molecular orbitals of HeH+ are formed from a linear combination of a 1*s*-atomic orbital of He and 1*s*-atomic orbital of H. Then the wave function of a molecular orbital of HeH+ may be written as

$$\psi = C_1 1s\text{He} + C_2\, 1s\text{H}$$

The secular equation is

$$\begin{vmatrix} \alpha\text{He} - E & \beta - SE \\ \beta - SE & \alpha\text{H} - E \end{vmatrix} = 0$$

where

$$\begin{aligned} \alpha\text{He} &= \langle\, 1s\text{He} \mid H \mid 1s\text{He} \,\rangle \\ \alpha\text{H} &= \langle\, 1s\text{H} \mid H \mid 1s\text{H} \,\rangle \\ \beta &= \langle\, 1s\text{H} \mid H \mid 1s\text{He} \,\rangle \\ S &= \langle\, 1s\text{H} \mid 1s\text{He} \,\rangle \end{aligned} \tag{1}$$

and $\hat{H}$ is the effective hamiltonian of the HeH+ system. For the sake of simplicity we neglect the overlap integral S in Eq. (1) as this is not going to affect the conclusion. The energy is given by

$$E = \tfrac{1}{2}\{(\alpha_{\text{He}} + \alpha_{\text{H}}) \pm [(\alpha_{\text{He}} - \alpha_{\text{H}})^2 + 4\beta^2]^{1/2}\}$$

For the bonding orbital one obtains

$$\frac{C_2}{C_1} = -\frac{\alpha\text{He} - \frac{1}{2}\{(\alpha\text{He} + \alpha\text{H}) - [(\alpha\text{He} - \alpha\text{H})^2 + 4\beta^2]^{1/2}\}}{\beta}$$

$$= -\frac{\alpha\text{He} - \alpha\text{H}}{2\beta} + \left[1 + \frac{(\alpha\text{He} - \alpha\text{H})^2}{4\beta^2}\right]^{1/2}$$

In this simple treatment αs are assumed equal to the ionisation potential of electron in the corresponding atomic orbitals of the isolated atoms.

$$\alpha\text{He} = -24.6 \text{ eV},\ \alpha\text{H} = -13.6 \text{ eV}$$

According to Mulliken's approximation

$$\beta = \frac{k}{2} S(\alpha\text{He} + \alpha\text{H}) = -38.2S,\ (k = 2.0)$$

Thus

$$\frac{\alpha\text{He} - \alpha\text{H}}{\beta} = \frac{0.28}{S}$$

One obtains

$$\frac{C_2}{C_1} = -\frac{0.28}{S} + \sqrt{1 + \frac{0.08}{S^2}}$$

The ratio C_2/C_1 can be shown to be less than unity for any value of S, hence,

$$C_1 > C_2$$

This means that the bond-electrons are clustered round the helium nucleus. Since the ionisation potential of He is greater than that of H, HeH+ is expected to dissociate more readily into He + H+ than into H + He+

3. One obtains the following expression for the electronic energy by the procedure described in Sec. 7.6.

$$E_{el} = 2E_1 + E_2 + J_{11} + 2J_{12} - K_{12}$$

where

$$J_{11} = \left\langle \sigma_g 1s(1)\sigma_g 1s(2) \left| \frac{1}{r_{12}} \right| \sigma_g 1s(1)\sigma_g 1s(2) \right\rangle$$

$$J_{12} = \left\langle \sigma_g 1s(1)\sigma_u 1s(2) \left| \frac{1}{r_{12}} \right| \sigma_g 1s(1)\sigma_u 1s(2) \right\rangle$$

$$K_{12} = \left\langle \sigma_g 1s(1)\sigma_u 1s(2) \left| \frac{1}{r_{12}} \right| \sigma_u 1s(1)\sigma_g 1s(2) \right\rangle$$

4. The electronic configuration of NH:

$$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^2,\ {}^3\Sigma-$$

5. According to Sec. 7.8, $\rho = 2\rho(1)$

$$\begin{aligned}\rho(1) = {} & (0.323)^2(\phi_{2s}^{\mathrm{Li}})^2 + (0.231)^2(\phi_{2p}^{\mathrm{Li}})^2 + (0.685)^2(\phi_{1s}^{\mathrm{H}})^2 \\ & +2\times 0.323\times 0.685(\phi_{2s}^{\mathrm{Li}}\cdot\phi_{1s}^{\mathrm{H}}) + 2\times 0.231\times 0.685(\phi_{2p}^{\mathrm{iL}}\cdot\phi_{1s}^{\mathrm{H}}) \\ & +2\times 0.323\times 0.231(\phi_{2s}^{\mathrm{Li}}\cdot\phi_{2p}^{\mathrm{Li}})\end{aligned}$$

$$\begin{aligned}\rho = 2\rho(1) = {} & 0.208(\phi_{2s}^{\mathrm{Li}})^2 + 0.106(\phi_{2p}^{\mathrm{Li}})^2 + 0.938(\phi_{1s}^{\mathrm{H}})^2 \\ & +0.886(\phi_{2s}^{\mathrm{Li}}\phi_{1s}^{\mathrm{H}}) + 0.632(\phi_{2p}^{\mathrm{Li}}\phi_{1s}^{\mathrm{H}}) + 0.298(\phi_{2s}^{\mathrm{Li}}\phi_{2p}^{\mathrm{Li}})\end{aligned}$$

Since $\int \rho\, d\tau = 2$, we have the charge distribution in LiH as

$$\begin{aligned}q_{\mathrm{Li}} &= 0.208 + 0.106 = 0.314 \\ q_{\mathrm{H}} &= 0.938 \\ q_{\mathrm{H,Li}} &= 0.886 \langle \phi_{2s}^{\mathrm{Li}} \mid \phi_{1s}^{\mathrm{H}} \rangle + 0.632 \langle \phi_{2p}^{\mathrm{Li}} \mid \phi_{1s}^{\mathrm{H}} \rangle \\ &= 0.886\times 0.5 + 0.632\times 0.5 \\ &= 0.759\end{aligned}$$

where $q_{\mathrm{H,Li}}$ means the distribution of electrons in the overlap region. It should be noted that ϕ_{2s}^{Li} and ϕ_{2p}^{Li} are orthogonal.

If we use Mulliken's gross populations then we regard the overlap density as belonging half to Li and half to H. The gross populations of valence electrons on the two atoms are

$$\begin{aligned}Q_{\mathrm{Li}} &= 0.314 + 1/2\times 0.759 \\ &= 0.693 \\ Q_{\mathrm{H}} &= 0.938 + 1/2\times 0.759 \\ &= 1.317\end{aligned}$$

If we consider that the MO of LiH is built up from overlapping a pair of orbitals on each atom, then we define a hybrid type of atomic orbitals of Li as

$$\phi_{\mathrm{Li}} = a\phi_{2s}^{\mathrm{Li}} + b\phi_{2p}^{\mathrm{Li}}$$

A linear combination of ϕ_{Li} and ϕ_{1s}^{H} gives the MO

$$\psi_{\mathrm{MO}} = \lambda\phi_{\mathrm{Li}} + 0.685\phi_{1s}^{\mathrm{H}}$$

$$\lambda(a\phi_{2s}^{\mathrm{Li}} + b\phi_{2p}^{\mathrm{Li}}) = 0.323\phi_{2s}^{\mathrm{Li}} + 0.231\phi_{2p}^{\mathrm{Li}}$$

Since $a^2 + b^2 = 1$ because the Li-orbital must be normalised, we have $\lambda a = 0.323$, $\lambda b = 0.231$.

One easily gets

$$a = 0.813 \qquad b = 0.582 \qquad \lambda = 0.397$$

Thus the hybrid atomic orbital of Li is given by

$$\phi_h^{\mathrm{Li}} = 0.813\phi_{2s}^{\mathrm{Li}} + 0.582\phi_{2p}^{\mathrm{Li}}$$

This means that in Li itself, 0.34 electrons are promoted from 2*s*-orbital to 2*p*-orbital before the bond is formed with H. This is possible because the 2*s*-2*p* energy separation in Li is small.

If q_{Li} and q_{H} were equal the bond would have been completely covalent. The bond would have become completely ionic as in $\mathrm{Li^+ H^-}$ if $q_{\mathrm{Li}} = 0$, $q_{\mathrm{H}} = 2$ corresponding to transfer of one electron from Li to H. McWeeny[1] (1965) introduced $1/2(q_A - q_B)$ as a measure of the fractional ionic character of the bond AB. So for LiH the fractional ionic character is given by

$$\frac{1}{2}(q_{\mathrm{H}} - q_{\mathrm{Li}}) = \frac{1}{2}(0.938 - 0.314) = 0.312$$

If we use Mulliken's gross populations of valence electrons this measure remains invariant. Thus, one may say that LiH has 31% ionic character.

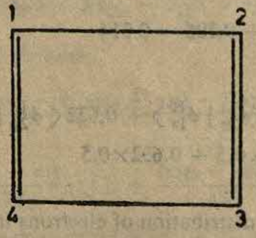
$$\mathrm{Li^{+0.312}{-}H^{-0.312}}$$

The two core electrons in Li simply screen two units of its nuclear charge.

6. $\mathrm{Na^+Cl^-}$ ($R = 9.26\times10^{-8}$ cm), $\mathrm{Li^+F^-}$ ($R = 7.7\times10^{-8}$ cm), $\mathrm{Na^+F^-}$ ($R = 8.8\times10^{-8}$ cm) $\mathrm{Li^+Cl^-}$ ($R = 7.9\times10^{-8}$ cm.)

Chapter 8

1.



The secular determinant is

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

which expands to

$$x^4 - 4x^2 = 0$$

or

$$x = 0, 0, \pm 2$$

Therefore, the energy levels in the order of increasing energy are

$$E_1 = \alpha + 2\beta$$
$$E_2 = E_3 = \alpha$$
$$E_4 = \alpha - 2\beta$$

---

[1] M. Klessinger and R. McWeeny, *J. Chem. Phys.*, 42, 3343, (1965)

Hence

$$E\pi = 4\alpha + 4\beta$$

$$D{\cdot}E = 0$$

Since the highest occupied orbital in cyclobutadiene is doubly degenerate, one can construct both the singlet and triplet states. According to Hund's rule the lowest state is triplet.

2. See Eqs. (8.53) for π-molecular orbitals of butadiene. For lowest excited configuration (i.e. $\psi_1^2\psi_2^1\psi_3^1$).

$$p_{12} = p_{34} = 2\times0.375\times0.607 + 1\times0.607\times0.375 + 1\times0.607\times(-0.375)$$
$$= 0.456$$
$$p_{23} = 2\times0.607\times0.607 - 1\times0.375\times0.375 + 1\times0.375\times0.375$$
$$= 0.720.$$

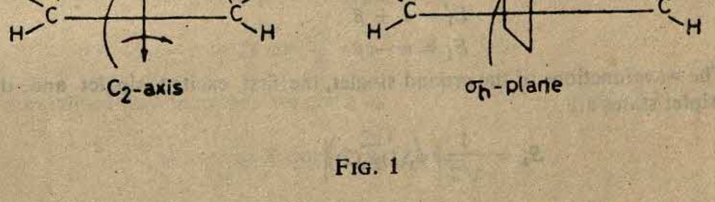
The results show that the central bond is shorter than the end bonds.

For the butadiene anion with the configuration $\psi_1^2\psi_2^2\psi_3^1$,

$$p_{12} = p_{34} = 2\times0.375\times0.607 + 2\times0.375\times0.607 + 1\times0.607\times(-0.375)$$
$$= 0.684$$
$$p_{23} = 2\times0.607\times0.607 + 2\times0.375\times(-0.375) + 1\times(-0.375)\times(-0.375)$$
$$= 0.547$$

This shows that the bond-orders are nearly equal.

3. In the conversion of cyclopropyl to allyl systems (radical or ions) σ and σ^* orbitals of 1-3 bond and π-orbital on 2-position in cyclopropyl pass adiabatically to three π-molecular orbitals of allyl [i.e. $\psi_1\psi_2$ and ψ_3; see Eqs. (8.47) and (8.48)]

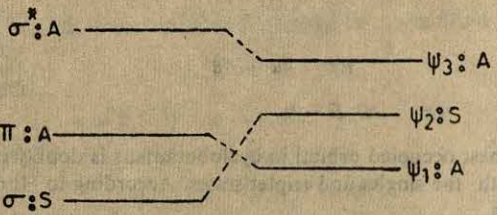


C_2-axis

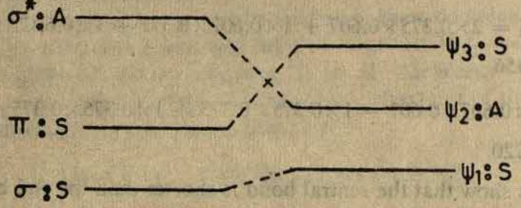
σ_h-plane

FIG. 1

How these two sets of orbitals are correlated depend on whether the reaction proceeds in conrotatory or disrotatory mode. For the conrotatory route, both the reactant and product maintain a two-fold axis (C_2-axis) of symmetry while in the disrotatory mode, a symmetry plane (σ_h-plane) perpendicular to the molecular plane is maintained (see Fig. 1). By a similar procedure described in Sec. 8.5 one obtains the following correlation diagrams for the conrotatory and disrotatory modes, where the symbols S and A refer to 'symmetric' and 'antisymmetric' with respect to whatever symmetry operation is applicable.



For conrotatory mode



For disrotatory mode

Clearly, the lowest energy configuration σ^2 of cyclopropyl cation correlates with the ground state configuration ψ_1^2 of allyl cation for disrotatory mode and with higher-energy configuration ψ_2^2 of allyl cation for conrotatory mode. It seems, therefore, that the disrotatory route is energetically favourable for thermal interconversion of cyclopropyl cation to allyl cation. As to the photochemical transformations, the first excited state $\sigma\pi$ correlates more favourably with $\psi_1^1\psi_2^1$ for the conrotatory route than with less stable configuration $\psi_1^1\psi_2^1$ for the disrotatory route. From similar arguments using the same correlation diagrams one expects that the thermal and photochemical interconversions of cyclopropyl anion to allyl anion follow the opposite routes. This establishes the Woodward-Hoffmann rule.

4. The two π-MOs of ethylene are

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \qquad \text{[see Sec. 8.5]}$$

The corresponding energies are

$$E_1 = \alpha + \beta$$

$$E_{\perp} = \alpha - \beta$$

The wavefunctions of the ground singlet, the first excited singlet and the lowest triplet states are

$$S_0 = \frac{1}{\sqrt{2}}\left| \psi_1(1)\overline{\psi_1}(2) \right|$$

$$S_1 = \frac{1}{2}[\,|\psi_1\overline{\psi_2}| - |\overline{\psi_1}\psi_2|\,]$$

$$T = \frac{1}{2}[\,|\psi_1\overline{\psi_2}| + |\overline{\psi_1}\psi_2|\,] \qquad \text{[see Sec. 7.10]}$$

The energies of these states are

$$E(S_0) = 2E_1 + J_{11}$$

$$E(S_1) = E_1 + E_2 + J_{12} + K_{12}$$

$$E(T) = E_1 + E_2 + J_{12} - K_{12}$$

$$J_{11} = \iint \psi_1(1)\psi_1(1) \left|\frac{1}{r_{12}}\right| \psi_1(2)\psi_1(2)\, d\tau_1\, d\tau_2$$

$$= \frac{1}{2}[\langle \phi_1\phi_1 \mid \phi_1\phi_1 \rangle + \langle \phi_1\phi_1 \mid \phi_2\phi_2 \rangle]$$

where the differential overlap ($\phi_1\phi_2 \approx 0$) is neglected. One obtains

$$J_{11} = J_{22} = J_{12} = \frac{1}{2}[\langle \phi_1\phi_1 \mid \phi_1\phi_1 \rangle + \langle \phi_1\phi_1 \mid \phi_2\phi_2 \rangle]$$

$$K_{12} = \frac{1}{2}[\langle \phi_1\phi_1 \mid \phi_1\phi_1 \rangle - \langle \phi_1\phi_1 \mid \phi_2\phi_2 \rangle]$$

The two-centre integrals is obtained for $R < 2.8$ Å by Eq. (8.88)

$$\langle \phi_1\phi_1 \mid \phi_1\phi_1 \rangle = 10.53 \text{ eV}$$

$$\langle \phi_1\phi_1 \mid \phi_2\phi_2 \rangle = 7.38 \text{ eV}$$

$$K_{12} = 1.57 \text{ eV}$$

$$\Delta E = E(S_1) - E(S_0) = E_2 - E_1 + J_{12} - J_{11} + K_{12}$$

$$= E_2 - E_1 + K_{12} = -2\beta + K_{12}$$

$$= +7.6 \text{ eV}$$

$$\Delta E = E(T) - E(S_0) = E_2 - E_1 - K_{12} = -2\beta - K_{12}$$

$$= 4.4 \text{ eV}$$

5. The energy levels are given by [Sec. 8.6]

$$E = \alpha + 2\beta \cos \frac{2J\pi}{N}$$

For $N = 6$, the possible values of J are

$$J = 0, \pm 1, \pm 2, +3$$

When $J = 0$, $\quad E_1 = \alpha + 2\beta$

$$J = \pm 1 \quad E_2 = \alpha + 2\beta \cos \frac{2\pi}{6} \cdot [\cos(-\theta) = \cos\theta]$$

$$= \alpha + \beta \text{ (doubly degenerate)}$$

$$J = \pm 2 \quad E_3 = \alpha + 2\beta \cos \frac{4\pi}{6}$$

$$= \alpha - \beta \text{ (doubly degenerate)}$$

$$J = +3 \quad E_4 = \alpha + 2\beta \cos \frac{6\pi}{6} = \alpha - 2\beta$$

The normalised wavefunctions are given by

$$\psi = \frac{1}{\sqrt{N}} \sum_r \exp\left(i\, \frac{2\pi J}{N} r\right) \cdot \phi_r$$

where ϕ_r is the atomic orbital on the r^{th} atom

Since J can be positive and negative integers we write

$$\psi_J = \frac{1}{\sqrt{6}} \sum_r \exp\left(i \frac{2\pi J}{6} r\right) \cdot \phi_r$$

$$\psi_{-J} = \frac{1}{\sqrt{6}} \sum_r \exp\left(-i \frac{2\pi J}{6} r\right) \cdot \phi_r$$

In terms of the real coefficients

$$\psi_J = \sum_r C_r^J \phi_r \tag{1}$$

One can write

$$\psi_J = A\psi_J + B\psi_{-J} \tag{2}$$

where A and B are arbitrary constants.

By comparing Eq. (1) and (2), one writes

$$\begin{aligned}
C_r^J &= A \exp\left(+i\frac{2\pi J}{6}r\right) + B \exp\left(-i\frac{2\pi J}{6}r\right) \\
&= A\left[\cos\frac{2\pi J}{6}r + i\sin\frac{2\pi J}{6}r\right] \\
&\quad + B\left[\cos\frac{2\pi J}{6}r - i\sin\frac{2\pi J}{6}r\right] \\
&= (A + B)\cos\frac{2\pi J}{6}r + (A - B)i\sin\frac{2\pi J}{6}r \\
&= D_1^J\cos\frac{2\pi J}{6}r + D_2^J\sin\frac{2\pi J}{6}r
\end{aligned}$$

where $D_1^J = (A + B)$, $D_2^J = (A - B)i$ and now only positive values of J need to be considered. When $J = 0$, only D_1^J coefficients need to be considered. While for $J = 1, 2$, etc., we obtain degenerate MOs and their coefficients are determined from both D_1^J and D_2^J.

$$J = 0; \quad \psi(J = 0) = D_1^0(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

Since

$$\int \psi^2(J = 0)\, d\tau = 1$$

we have

$$(D_1^0)^2[1 + 1 + 1 + 1 + 1 + 1] = 1$$

$$D_1^0 = \frac{1}{\sqrt{6}}$$

$$\psi(J = 0) = \frac{1}{\sqrt{6}}[\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6]$$

$$\begin{aligned}
\psi(J = 1) &= D_1^J\left[\left(\cos\frac{2\pi}{6}\cdot 1\right)\phi_1 + \left(\cos\frac{2\pi}{6}\cdot 2\right)\phi_2 + \left(\cos\frac{2\pi}{6}\cdot 3\right)\phi_3\right. \\
&\quad \left. + \left(\cos\frac{2\pi}{6}\cdot 4\right)\phi_4 + \left(\cos\frac{2\pi}{6}\cdot 5\right)\phi_5 + \left(\cos\frac{2\pi}{6}\cdot 6\right)\phi_6\right] \\
&= D_1^J[1/2\phi_1 - 1/2\phi_2 - \phi_3 - 1/2\phi_4 + 1/2\phi_5 + \phi_6]
\end{aligned}$$

Since $\int \psi(J = 1)^2\, d\tau = 1$, we have

$$(D_1^{(1)})^2\left[\frac{1}{4} + \frac{1}{4} + 1 + \frac{1}{4} + \frac{1}{4} + 1\right] = 1$$

$$3(D_1^1)^2 = 1$$

$$D_1^{(1)} = \frac{1}{\sqrt{3}}$$

$$\psi(J = 1) = \frac{1}{2\sqrt{3}}[\phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5 + 2\phi_6]$$

The other component of the degenerate MO is given as

$$\psi(J = 1) = D_2^{(1)}\Big[\Big(\sin\frac{2\pi}{6}\cdot 1\Big)\phi_1 + \Big(\sin\frac{2\pi}{6}\cdot 2\Big)\phi_2 + \Big(\sin\frac{2\pi}{6}\cdot 3\Big)\phi_3$$

$$+ \Big(\sin\frac{2\pi}{6}\cdot 4\Big)\phi_4 + \Big(\sin\frac{2\pi}{6}\cdot 5\Big)\phi_5 + \Big(\sin\frac{2\pi}{6}\cdot 6\Big)\phi_6\Big]$$

$$= D_2^{(1)}[0.866\phi_1 + 0.866\phi_2 - 0.866\phi_4 - 0.866\phi_5]$$

$$= 0.866D_2^{(1)}[\phi_1 + \phi_2 - \phi_4 - \phi_5]$$

After normalisation we obtain

$$\psi(J = 1) = \frac{1}{2}[\phi_1 + \phi_2 - \phi_4 - \phi_5]$$

The other three MOs are given as

$$\psi(J = 2) = \frac{1}{2}(\phi_1 - \phi_2 + \phi_4 - \phi_5)$$

$$\psi(J = 2) = \frac{1}{2\sqrt{3}}(\phi_1 + \phi_2 - 2\phi_3 + \phi_4 + \phi_5 - 2\phi_6)$$

$$\psi(J = 3) = \frac{1}{\sqrt{6}}[\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6]$$

The total π-electron energy in benzene is $(2E_1 + 4E_2)$, i.e., $6\alpha + 8\beta$.
The total π-electron energy of three ethylene molecules is $6\alpha + 6\beta$.
The delocalisation energy (*DE*) for neutral benzene is

$$DE = 6\alpha + 8\beta - 6\alpha - 6\beta = 2\beta$$

The total π-electron energy of benzene cation is

$$(2E_1 + 3E_2), \text{ i.e., } 5\alpha + 7\beta$$

The total π-electron energy of two neutral ethylene and one ethylene cation is $5\alpha + 5\beta$. Hence,

$$DE = 5\alpha + 7\beta - 5\alpha - 5\beta = 2\beta$$

The total π-electron energy of benzene anion is

$$(2E_1 + 4E_2 + E_3), \quad \text{i.e., } 7\alpha + 7\beta$$

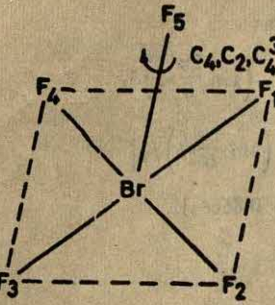
The total π-electron energy of two neutral ethylene and one ethylene anion is $7\alpha + 5\beta$.

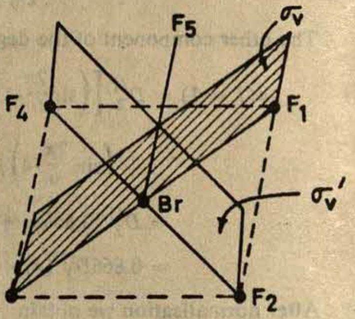
$$DE = 7\alpha + 7\beta - 7\alpha - 5\beta = 2\beta$$

Chapter 9

1. ICl_4^-	D_4h
C_2H_4	D_2h
C_4H_8	D_4h
C_5H_5N	C_{2v}
1 : 3 : 5 Trichlorobenzene	D_{3h}
CO_2	$D\infty h$
CCl_4	Td

2.





Multiplication table for C_{4v}

First operation				*Second operation*				
	E	C_4	C_4^3	C_2	σ_v	σ_v'	σd	$\sigma d'$
E	E	C_4	C_4^3	C_2	σ_v	σ_v'	σd	$\sigma d'$
C_4	C_4	C_2	E	C_4^3	σd	$\sigma d'$	σ_v'	σ_v
C_4^3	C_4^3	E	C_2	C_4	$\sigma d'$	σd	σ_v	σ_v'
C_2	C_2	C_4^3	C_4	E	σ_v'	σ_v	$\sigma d'$	σd
σ_v	σ_v	σd	$\sigma d'$	σ_v	E	C_2	C_4^3	C_4
σ_v'	σ_v'	$\sigma d'$	σd	σ_v	C_2	E	C_4	C_4^3
σd	σd	σ_v'	σ_v	$\sigma d'$	C_4	C_4^3	E	C_2
$\sigma d'$	$\sigma d'$	σ_v	σ_v'	σd	C_4^3	C_4	C_2	E

That elements like σ_v and σ_v' form a class can be shown as

$$E^{-1}{}_{\sigma_v}E = \sigma_v$$

$$C_4^{-1}\sigma_v C_4 = C_4^3\sigma d = \sigma_v$$

$$(C_4^3)^{-1}\sigma_v C_4^3 = C_4\sigma d' = \sigma_v$$

$$\sigma d^{-1}\sigma_v \sigma d = \sigma d C_4^3 = \sigma_v$$

$$C_2^{-1}\sigma v C_2 = \sigma v$$

$$\sigma_v^{-1}\sigma v\, \sigma v = \sigma v$$

$$(\sigma v')^{-1}\sigma v\, \sigma v' = \sigma v' C_2 = \sigma v$$

$$(\sigma d')^{-1}\sigma v\, \sigma d = \sigma d' C_4^3 = \sigma v'$$

Similarly, one can show that $\sigma d'$ and σd form a class, C_4 and C_4^3 form another class, and C_2 forms a class by itself while E forms a class for all groups.

There are therefore five classes as:

$$E,\ C_4 \text{ and } C_4^3,\ C_2,\ \sigma d \text{ and } \sigma d',\ \sigma v \text{ and } \sigma v'$$

One can write the C_{4v} group as

$$E,\ 2C_4,\ C_2,\ 2\sigma v,\ 2\sigma d$$

The number of classes is equal to the number of the irreducible representations. Suppose, l_1, l_2, l_3, l_4 and l_5 are the dimensions of the five representations, then

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 + l_5^2 = 8$$

Therefore, there are four representations of dimension one and one of dimension two.

3. From the D_6h character table we have

$$\begin{array}{lcccccccc} & E, & 2C_6, & 2C_3, & C_2, & 3C_2', & 3C_2'', & i, & 2C_3, \\ \chi(E_{1u}\times E_{1u}) & 4 & +1 & +1 & +4 & 0 & 0 & +4 & +1 \end{array}$$

$$\begin{array}{cccc} 2S_6, & \sigma h, & 3\sigma d, & 3\sigma v \\ +1 & +4 & 0 & 0 \end{array}$$

Following the usual treatment shown in the text.

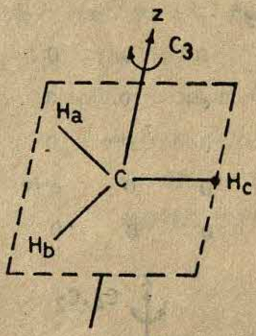
$$\begin{aligned} a(A_{1g}) &= \frac{1}{24}[4\times1 + 2\times1\times1 + 2\times1\times1 + 4\times1 + 3\times0\times1 + 3\times0\times1 \\ &\quad +4\times1\times1 + 2\times1\times1 + 2\times1\times1 + 4\times1\times1 + 3\times0\times1 + 3\times0\times1] \\ &= 1 \end{aligned}$$

$$a(A_{2g}) = 1/24[4 + 2 + 2 + 4 + 4 + 2 + 2 + 4] = 1$$

$$a(E_{2g}) = 1/24[8 - 2 - 2 + 8 + 8 - 2 - 2 + 8] = 1$$

$$E_{1u}\times E_{1u} = A_{1g} + A_{2g} + E_{2g}$$

4. In methyl radical, there are three hydrogen $1s$ orbitals, one carbon $2s$-orbital and three carbon $2p$-orbitals, i.e., $2px$, $2py$ and $2pz$.



There is usually no need to write the full matrix representation. It is sufficient to be able to write down the character. If a symmetry operator completely moves a function away from its original position this will correspond to a zero on the diagonal of the matrix and therefore does not contribute to the character. We can therefore construct the following table which shows the bases for the representations. And the reducible one is decomposed into irreducible components by the usual procedure. It is to be noted, however, that a C_3 operation on $2p_x$ or $2p_y$ gives a mixture of these two orbitals.

TABLE

Bases		E	σh	$2C_3$	$2S_3$	$2C_2'$	$3\sigma v$	
$1sa$, $1sb$, $1sc$	Γ_1	3	3	0	0	1	1	$\Gamma_1 = A_1' + E'$
$2s$	Γ_2	1	1	1	1	1	1	$\Gamma_2 = A_1'$
$2pz$	Γ_3	1	−1	1	−1	−1	1	$\Gamma_3 = A_2''$
$2px$, $2py$	Γ_4	2	2	−1	−1	0	0	$\Gamma_4 = E'$

This table shows that the 2*s*-orbital of carbon forms bonding and antibonding molecular orbitals with the A_1' combination of the hydrogen orbitals. Similarly, the 2*px* and 2*py* and the E' combination of the hydrogen orbitals give bonding and antibonding E' molecular orbitals while the 2*pz*-orbital will be nonbonding. The methyl radical has seven valence electrons, six of them fill the bonding molecular orbitals and the seventh one occupies the nonbonding orbital which has the A_2'' symmetry.

5. We shall first consider how the five *d*-orbitals transform under the D_4 operation. The 3*d*-orbitals are characterised by the quantum numbers $n = 3$, $l = 2$ and $m = +2, +1, 0, -1, -2$. The orbitals are given as

$$\psi_{3,2,m} = R_{3\cdot2}(r)P_2^{|m|}(\cos\theta)\frac{e^{im\phi}}{\sqrt{2\pi}}$$

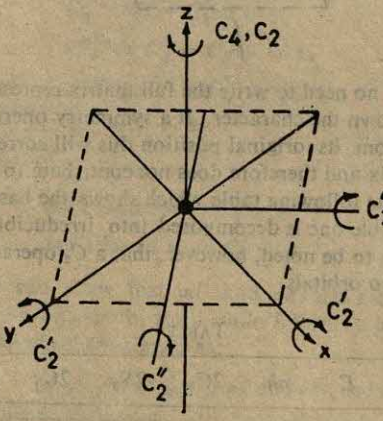
Let us consider a *d*-orbital centred on a metal atom in a square configuration as shown in the figure.

The most general rotation is that around any arbitrary axis by an angle, say φ.

$$\begin{aligned}
C(\varphi)\psi_{3,2,2} &= R_{3\cdot2}(r)P_2^2(\cos\theta)1/\sqrt{2\pi}e^{i2(\phi+\varphi)}\\
&= e^{i2\varphi}\cdot\psi_{3,2,2}\\
C(\varphi)\psi_{3,2,1} &= e^{i\varphi}\cdot\psi_{3,2,1}\\
C(\varphi)\cdot\psi_{3,2,0} &= e^{i0\varphi}\cdot\psi_{3,2,0}\\
C(\varphi)\psi_{3,2,-1} &= e^{-i\varphi}\cdot\psi_{3,2,-1}\\
C(\varphi)\psi_{3,2,-2} &= e^{-i2\varphi}\cdot\psi_{3,2,-2}
\end{aligned}$$

The $C(\varphi)$ matrix is given by

$$\begin{vmatrix}
e^{i2\varphi} & 0 & 0 & 0 & 0\\
0 & e^{i\varphi} & 0 & 0 & 0\\
0 & 0 & e^{i0\varphi} & 0 & 0\\
0 & 0 & 0 & e^{-i\varphi} & 0\\
0 & 0 & 0 & 0 & e^{-2i\varphi}
\end{vmatrix}$$



Hence the character,

$$\begin{aligned}
\chi &= e^{2i\varphi} + e^{i\varphi} + e^{i0\varphi} + e^{-i\varphi} + e^{-2i\varphi}\\
&= 2\cos 2\varphi + 2\cos\varphi + 1 \quad [\text{since } e^{i\varphi} + e^{-i\varphi} = 2\cos\varphi]
\end{aligned}$$

For the C_4 operation, $\varphi = \pi/2$, $\chi(C_4) = -1$
For the C_2 operation, $\varphi = \pi$, $\chi(C_2) = +1$
The characters of the representations spanned by the five d-orbitals under the operations of D_4 are given by

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
Γ	5	-1	$+1$	$+1$	$+1$

The above reducible representation Γ is decomposed into irreducible components of D_4 by the usual procedure:

$$\Gamma = A_1 + B_1 + B_2 + E$$

The group D_4h has in addition to the above elements of D_4, the inversion, i, $2i \times C_4$, $i \times C_2$, $2i \times C_2'$ and $2i \times C_2''$ elements. Since all the five d-orbitals are symmetric under reflection in their symmetry centre, we can get only the symmetric representations in the D_4h group. Therefore, in the D_4h point group, the five d-orbitals have the symmetries, A_{1g}, B_{1g}, B_{2g}, E_g.

6. The three π-MOs of the allyl system are shown in the figure

$$\psi_1 = 1/2\cdot\phi_1 + 1/\sqrt{2}\cdot\phi_2 + 1/2\cdot\phi_3$$

$$\psi_2 = 1/\sqrt{2}\cdot\phi_1 - 1/\sqrt{2}\cdot\phi_3$$

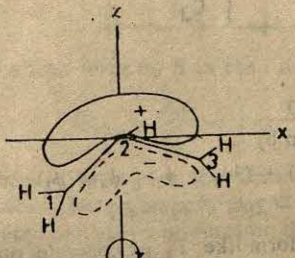
$$\psi_3 = 1/2\phi_1 - 1/\sqrt{2}\cdot\phi_2 + 1/2\phi_3$$

$$C_2\psi_1 = -1/2\cdot\phi_3 - 1/\sqrt{2}\cdot\phi_2 - 1/2\cdot\phi_1 = -\psi_1$$

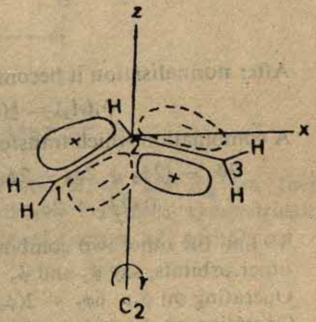
$$C_2\psi_2 = -1/\sqrt{2}\cdot\phi_3 + 1/\sqrt{2}\cdot\phi_1 = \psi_2$$

$$C_2\psi_3 = -1/2\phi_3 + 1/\sqrt{2}\cdot\phi_2 - 1/2\cdot\phi_1 = -\psi_3$$

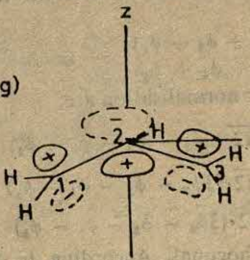
$\sigma v(xz)\psi_1 = -\psi_1$ $\qquad$ $\sigma v(yz)\psi_1 = \psi_1$
$\sigma v(xz)\psi_2 = -\psi_2$ $\qquad$ $\sigma v(yz)\psi_2 = -\psi_2$
$\sigma v(xz)\psi_3 = -\psi_3$ $\qquad$ $\sigma v(yz)\psi_3 = \psi_3$



ψ_1: $\alpha + \sqrt{2}\beta$ (bonding)



ψ_2: α (nonbonding)



ψ_3: $\alpha - \sqrt{2}\beta$ (antibonding)

We therefore classify the π-MOs of the allyl system as

	E	$C_2(z)$	$\sigma v(xz)$	$\sigma v'(yz)$	
ψ_1	1	-1	-1	1	B_2
ψ_2	1	$+1$	-1	-1	A_2
ψ_3	1	-1	-1	$+1$	B_2

7. *Td* has $4C_3$ and $4C_3^2$ which make members of a class $8C_3$, three C_2 axes, i.e. $3C_2$, $3S_4$ and $3S_4^3$ make another class $6S_4$. Besides the above, it has six planes of reflection which are σd rather than σv. With the four hydrogen 1*s* orbitals as bases, we find the following reducible representation.

	E	$6S_4$	$3C_2$	$6\sigma d$	$8C_2$
Γ	4	0	0	2	1

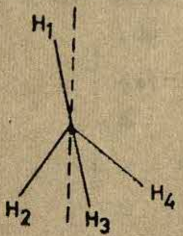
$$\Gamma = A_1 + T_2$$

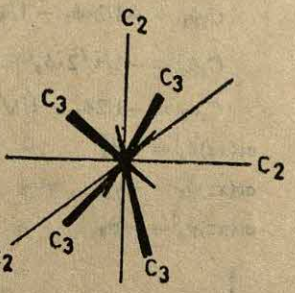
Let ϕ_1, ϕ_2, ϕ_3 and ϕ_4 be the four hydrogen orbitals.
Operating on ϕ_1 we get

	E	$6S_4$	$3C_2$	$6\epsilon d$	$8C_3$
ϕ_1	ϕ_1,	$2\phi_2 + 2\phi_3 + 2\phi_4$,	$\phi_2 + \phi_3 + \phi_4$,	$3\phi_1 + \phi_2 + \phi_3 + \phi_4$,	$2\phi_1 + 2\phi_2 + 2\phi_3 + 2\phi_4$

Obviously, the orbital with A_1 symmetry has the combination

$$\phi_1 + \phi_2 + \phi_3 + \phi_4$$





After normalisation it becomes

$$\psi_1(A_1) = \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

A combination which transforms like T_2 is given by

$$3\phi_1 - (2\phi_2 + 2\phi_3 + 2\phi_4) - (\phi_2 + \phi_3 + \phi_4) + (3\phi_1 + \phi_2 + \phi_3 + \phi_4)$$
$$+ 0.(2\phi_1 + 2\phi_2 + 2\phi_3 + 2\phi_4) = 6\phi_1 - 2(\phi_2 + \phi_3 + \phi_4) \quad (1)$$

To find the other two combinations which transform like T_2 we operate on two other orbitals, say ϕ_2 and ϕ_3.

Operating on ϕ_2: $6\phi_2 - 2(\phi_3 + \phi_4 + \phi_1)$ (2)

Operating on ϕ_3: $6\phi_3 - 2(\phi_2 + \phi_4 + \phi_1)$ (3)

Functions (1), (2) and (3) after normalisation are:

$$\psi_2 = \sqrt{1/12}\cdot(3\phi_1 - \phi_2 - \phi_3 - \phi_4)$$
$$\psi_3 = \sqrt{1/12}\cdot(3\phi_2 - \phi_3 - \phi_4 - \phi_1)$$
$$\psi_4 = \sqrt{1/12}\cdot(3\phi_3 - \phi_2 - \phi_4 - \phi_1)$$

But these functions are not orthogonal. According to Schmidt orthogonalisation procedure, we assume

$$\psi_3' = \psi_3 + C\psi_2$$

where ψ_3' is orthogonal to ψ_2, i.e.

$$\langle \psi_3' \mid \psi_2 \rangle = \langle \psi_3 \mid \psi_2 \rangle + C \langle \psi_2 \mid \psi_2 \rangle = 0$$

$$\langle \psi_3 \mid \psi_2 \rangle = -1/3; \text{ hence } C = 1/3$$

$$\begin{aligned} \psi_3' = \psi_3 + 1/3\cdot\psi_2 &= 1/\sqrt{12}\cdot[3\phi_2 - \phi_3 - \phi_4 - \phi_1] \\ &\quad + 1/\sqrt{12}\cdot[\phi_1 - \phi_2/3 - \phi_2/3 - \phi_4/3] \\ &= 1/\sqrt{12}\cdot 4/3[2\phi_2 - \phi_3 - \phi_4] \end{aligned}$$

On normalisation,

$$\psi_3' = 1/\sqrt{6}\cdot(2\phi_2 - \phi_3 - \phi_4)$$

Lastly, we can orthogonalise ψ_4 to ψ_2 and ψ_3' and obtain

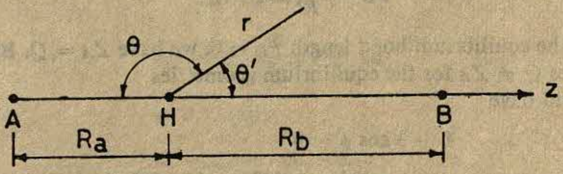
$$\psi_4' = 1/\sqrt{2}\cdot(\phi_3 - \phi_4)$$

Therefore, the three mutually orthogonal and normalised functions of T_2 symmetry are given as:

$$\psi_2 = 1/\sqrt{12}\cdot(3\phi_1 - \phi_2 - \phi_3 - \phi_4)$$
$$\psi_3' = 1/\sqrt{6}\cdot(2\phi_2 - \phi_3 - \phi_4)$$
$$\psi_4' = 1/\sqrt{2}\cdot(\phi_3 - \phi_4)$$

Chapter 11

1. The hydrogen bonded species is shown in the following figure.



The total force on H in the z direction is given by

$$F_{H,z} = \frac{Z_A}{R_a^2} - \int \rho_A \frac{\cos\theta'}{r^2}\, d\tau - \frac{Z_B}{R_b^2} + \int \rho_B \frac{\cos\theta'}{r^2}\, d\tau$$

where ρ_A and ρ_B are the electron densities on A and B, Z_A and Z_B are their nuclear charges respectively. We assume that the density on H is symmetrically placed and exerts no force on the proton. For spherical charges Q_A and Q_B on A and B respectively.

$$\int \rho_A \frac{\cos\theta'}{r^2}\, d\tau \cdot \approx \frac{Q_A}{R_a^2}$$

$$\int \rho_B \frac{\cos\theta'}{r^2}\, d\tau \cdot \approx \frac{Q_B}{R_b^2}$$

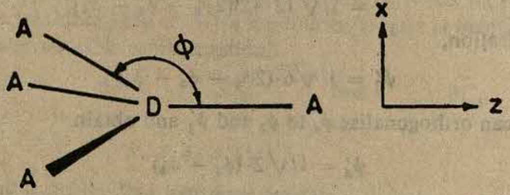
$$F_{H,z} = \frac{1}{R_a^2}(Z_A - Q_A) - \frac{1}{R_b^2}(Z_B] - Q_B)$$

Initially, for the free acid molecule HA of bond length R_a' we have

$$F^0_{H,z} = \frac{Z_A - Q_A}{R_a'^2}$$

Since there is no net force when the molecule has the equilibrium bond length, $Z_A = Q_A$. However, when R_b is finite the density on B exerts a resultant force on H away from A. This means that the value of $(Z_B - Q_B)/R_b^2$ becomes a negative number. In order that $F_{H,z} = 0$ for the equilibrium geometry of the hydrogen bonded system, R_a must be greater than R'_a. Thus, hydrogen bonding with base B leads to an increase of the bond length in HA over the free acid value.

2. Consider DA_4 as shown in the figure.



where one DA bond lies on the z axis and makes an angle ϕ with the other DA bonds. The net force on D in the z-direction is given by

$$F_{D,z} = -\frac{Z_D Z_A}{R^2} + \frac{Z_D Z_A}{R^2}(-3\cos\phi) + \frac{Z_D Q}{R^2} + \frac{Z_D Q}{R^2}\cdot 3\cos\phi$$

$$= \frac{Z_D}{R^2}(1 + 3\cos\phi)(Q - Z_A)$$

When Z stands for the nuclear charge and Q is the charge equivalent of the electronic force (see Eq. 11.27) on the nucleus D per unit positive charge by the electron-pair in DA. In a diatomic molecule DA, the net force on D is given by

$$F_D = \frac{Z_D}{R^2}(Z_A - Q)$$

and for the equilibrium bond length $F_D = 0$, we have $Z_A = Q$. But for polyatomic molecules $Q \neq Z_A$ for the equilibrium geometries.
We should have

$$1 + 3\cos\phi = 0$$

$$\cos\phi = -1/3 \qquad \phi = 109.5^\circ$$

Therefore, a non-planar molecule DA_4 with four equivalent DA bonds is a regular tetrahedron.

For DA_3^+, without any lone pair electrons but with three equivalent DA bonds we have

$$F_{D,z} = \frac{Z_D Z_A}{R^2} 3\cos(180 - \phi) + \frac{Z_D Q}{R^2} 3\cos\phi$$

$$= \frac{3Z_D}{R^2}\cos\phi(Q - Z_A)$$

Since $Q \neq Z_A$, for the equilibrium geometry $\cos\phi = 0$ hence $\phi = 90^\circ$. This means that all the three DA bonds must lie in the same plane.

3. The atomic force on nitrogen due to its lone pair is given as

$$f_N^{\text{atomic}} = -Z_N \int \rho(\mathbf{r}) \frac{\cos\theta}{r_N^2}\, d\tau$$

where

$$\rho(\mathbf{r}) = 2\psi_N^2 = 2[C_1^2\phi_{2s}^2 + C_2^2\phi_{2p}^2 + 2C_1C_2\phi_{2s}\cdot\phi_{2p}]$$

$$f_N^{\text{atomic}} = -2Z_N\Big[C_1^2\int \phi_{2s}^2 \frac{\cos\theta_N}{r_N^2}\,d\tau + C_2^2\int \phi_{2p}^2\cdot\frac{\cos\theta_N}{r_N^2}\,d\tau$$

$$+2C_1C_2\int \phi_{2s}\phi_{2p}\cdot\frac{\cos\theta_N}{r_N^2}\,d\tau\ \Big]$$

$$= -2Z_N\times 1.063\int \phi_{2s}\phi_{2p}\,\frac{\cos\theta_N}{r_N^2}\,d\tau$$

where the first two integral vanish because the atomic orbitals are centrosymmetric.

The Slater orbitals are

$$\phi_{2s} = \left[\frac{\alpha^5}{3\pi}\right]^{1/2}\cdot r\exp(-\alpha r)$$

$$\phi_{2p} = \left[\frac{\alpha^5}{3\pi}\right]^{1/2}\cdot r\cos\theta\exp(-\alpha r)$$

$$\alpha = 1.95$$

Consider the integral

$$\int \phi_{2s}\cdot\phi_{2p}\cdot\frac{\cos\theta_N}{r_N^2}\,d\tau = \frac{\alpha^5}{\sqrt{3}(\pi)}\iiint \exp(-2\alpha r)r^2\cdot\cos\theta$$

$$\times\frac{\cos\theta}{r^2}r^2\,dr\sin\theta\,d\theta\,d\phi$$

$$= \frac{\alpha^5}{\pi\sqrt{3}}\int_0^\infty \exp(-2\alpha r)r^2\cdot dr\int_0^\pi \cos^2\theta\sin\theta\,d\theta\int_0^{2\pi}d\phi$$

$$= \frac{\alpha^5}{\pi\sqrt{3}}\cdot\frac{2}{(2\alpha)^3}\cdot\frac{2}{3}\cdot 2\pi$$

$$= 0.73\ \text{(au)}$$

$$f_N^{\text{atomic}} = -2Z_N\times 1.063\times 0.73$$

$$= -10.86\ \text{(au)} \qquad [\text{if } Z_N = 7.0\ \text{(au)}]$$

$$1\ \text{au. of force} = e^2/4\pi\epsilon_0 a_0^2 = 8.2388\times 10^{-8}\ \text{N}$$

4. The $1\sigma_g$ and $1\sigma_u$ MO's of He_2 are given as

$$1\sigma_g: \frac{\phi_a+\phi_b}{\sqrt{2+2s}} \qquad 1\sigma_u: \frac{\phi_a-\phi_b}{\sqrt{2-2s}}$$

where ϕ's are the $1s$ atomic orbitals and $s = \langle \phi_a \mid \phi_b\rangle$

$$\rho = 2(1\sigma_g)^2 + 2\,(1\sigma_u)^2$$

$$= \frac{\phi_a^2+\phi_b^2+2\phi_a\cdot\phi_b}{1+s} + \frac{\phi_a^2+\phi_b^2-2(\phi_a\cdot\phi_b)}{1-s}$$

$$= \frac{2\phi_a^2+2\phi_b^2-4(\phi_a\cdot\phi_b)s}{1-s^2}$$

$$= 2\phi_a^2+2\phi_b^2-4\phi_a\cdot\phi_b s + 2s^2\}\phi_a^2+\phi_b^2\} + \dots$$

where we neglect terms higher than second-order in the overlap. The electronic force on He in He_2 is given as

$$
\begin{aligned}
Z_{He}\int \rho\frac{\cos\theta_a}{r_a^2}\,d\tau &= Z_{He}\Big[2\int\phi_a^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau + 2\int\phi_b^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau \\
&\quad -4S\int\phi_a\phi_b\,\frac{\cos\theta_a}{r_a^2}\,d\tau + 2s^2\Big\{\int\phi_a^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau \\
&\quad + \int\phi_b^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau\Big\}\Big] \\
&= Z_{He}\Big[(2+2s^2)\int\phi_b^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau - 4s\int\phi_a\phi_b\,\frac{\cos\theta_a}{r_a^2}\,d\tau\Big] \\
&= Z_{He}\Big[(2+2s^2)\int\phi_b^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau - \frac{4s^2}{2}\Big\{\int\phi_a^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau \\
&\quad + \int\phi_b^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau\Big\}\Big] \quad \text{(Using Mulliken's approximation)} \\
&= Z_{He}\cdot 2\int\phi_b^2\,\frac{\cos\theta_a}{r_a^2}\,d\tau \\
&= Z_{He}2\cdot\Big[\frac{1}{R^2}\{1-(1+2Q+2Q^2)\exp(-2Q)\}\Big]
\end{aligned}
$$

where $Q = \beta R$, β being the orbital exponent of the 1s-orbital [see R.F.W. Bader and G. Jones, *Canad. J. Chem.*, **39**, 1253, 1961]

$$\phi_b = \left[\frac{\beta^3}{\pi}\right]^{1/2}\cdot\exp(-\beta r_b)$$

For the He-atom, $\beta = 1.69$ [see Chapter 6, Sec. 6.2]. The net force on He is given by

$$
\begin{aligned}
F_{He} &= \frac{Z_{He}Z_{He}}{R^2} - Z_{He}\int\rho(\mathbf{r})\,\frac{\cos\theta_a}{r_a^2}\,d\tau \\
&= \frac{4}{R^2} - 2\times 2\Big[\frac{1}{R^2}\Big\{1-(1+2Q+2Q^2)\exp(-2Q)\Big\}\Big] \\
&= +\frac{4}{R^2}(1+2Q+2Q^2)\cdot\exp(-2Q)
\end{aligned}
$$

This net force is thus positive hence, repulsive at all values of R

R(au)	F_{He}(au)
4.0	3.4×10^{-5}
5.0	1.18×10^{-6}
6.0	4.0×10^{-8}
7.0	4.4×10^{-9}
8.0	4.4×10^{-11}

1 au of force = 8.2388×10^{-8} N

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Energy Conversion Table

	a.u.	eV	cm^{-1}	kcal/mole	erg
1 a.u.	1	27.2	2.1947×10^{5}	6.277×10^{4}	4.358×10^{-11}
1 eV	0.0367	1	8.066×10^{3}	23.07	1.602×10^{-12}
1 cm^{-1}	4.556×10^{-6}	1.2398×10^{-4}	1	2.86×10^{-3}	1.9862×10^{-16}
1 kcal/mole	1.593×10^{-3}	0.0433	3.4964×10^{2}	1	6.9446×10^{-14}
1 erg molecule^{-1}	2.294×10^{10}	6.24×10^{11}	5.035×10^{15}	1.44×10^{13}	1

Fundamental Constants

Charge on electron	$c = 4.8 \times 10^{-10}$ csu
Velocity of light	$c = 2.998 \times 10^{10}$ cm/sec
Planck's constant	$h = 6.624 \times 10^{-27}$ crg sec
Mass of electron	$m_e = 9.107 \times 10^{-28}$ gm
Mass of proton	$m_p = 1.673 \times 10^{-24}$ gm
Boltzmann constant	$k = 1.4 \times 10^{-16}$ erg degree^{-1}
Rydberg constant	$R = 109737$ cm^{-1} (for infinite nuclear mass)
Bohr radius	$a_0 = 0.529 \times 10^{-8}$ cm
Bohr magneton	$\beta = 0.927 \times 10^{-20}$ crg gauss^{-1}

Conversion Table in SI Units

Physical quantity	Old unit	Value in SI units
Distance	Centimetre	Metre, m 1 cm = 10^{-2} metre
Energy	Calorie (thermo-chemical)	4.184 J (joule)
	Electron volt—eV	1.602×10^{19}J
	Erg	10^{-7}J
	Wave number, cm^{-1}	1.986×10^{-23}J
Force	Dyne	10^{-5}N (Newton)
Pressure	Atmosphere	1.013×10^{5} Pa (Pascal)
	torr = mm Hg	133.3 Pa
Frequency	Cycle per second	1 Hz (hertz)
Relative permittivity	Dielectric constant	1
Temperature	°C and °K	1 K (kelvin) 0°C = 273.2K
Mass	Gram	10^{-3} kg (kilogram)
Charge of an electron	4.8×10^{-10}esu	1.6021×10^{-19}C
Dipole moment	Debye-D	3.334×10^{-30}C.m.

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INTRODUCTORY QUANTUM CHEMISTRY
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Most of the chapters in this edition have been revised and new material has been added to keep pace with the revised curriculum in various universities. A new chapter on semiempirical and ab initio molecular orbital theories is included. Its relationship to chemical bonding and role in understanding molecular physics have been emphasised. Lasers and other mechanisms of electronic transitions are also introduced. This will help the students in understanding the recent trends in spectroscopy and the use of lasers in chemistry. A brief outline of the concept of tensors is given and its application in rotational spectroscopy discussed.

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The book is primarily intended to serve as a basic text for students of chemistry for courses on quantum chemistry and chemical bonding at the postgraduate level. It will also be useful for research workers in physical chemistry.

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